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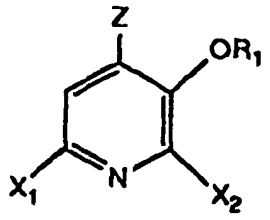
(54) Title: PYRIDINE-MICROBICIDES


(57) Abstract

Novel substituted pyridine derivatives of general formula (I) in which: $X_1$ is halogen or hydrogen, $X_2$ is halogen; Z is -C(=O)A, -C(=S)A or $-CH(OR_2)_2$, and in which A is hydrogen, $OR_3$, $SR_3$, $NR_4R_5$, $NHOR_6$, $-ON=CR_7R_8$ or $NH-N(=C)_n(R_9)R_{10}$; $R_1$ is as defined in the description. The novel active compounds possess plant-protecting properties and are particularly suitable for protecting plants preventatively against infestation with phytopathogenic microorganisms such as fungi, bacteria and viruses.

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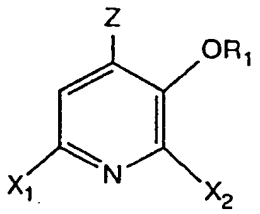
# Pyridine - microbicides

The present invention relates to novel substituted pyridine derivatives of the formula I below. The invention also relates to the preparation of these substances and to compositions which comprise a compound of the formula I as an active compound. The invention furthermore relates to the preparation of the said compositions and to the use of the active compounds or the compositions for protecting plants against infestation with pernicious microorganisms, for example fungi, bacteria and viruses.

The compounds according to the invention are of the general formula I




(I)

in which:
$X_1$ is halogen or hydrogen,
$X_2$ is halogen;
Z is -C(=O)A, -C(=S)A or -$CH(OR_2)_2$, and in which
A is hydrogen, $OR_3$, $SR_3$, $NR_4R_5$, $NHOR_6$, -$ON=CR_7R_8$ or NH-$N(=C)_n(R_9)R_{10}$;
$R_1$ is hydrogen; $C_1$-$C_4$alkyl which can be unsubstituted or substituted by phenyl, -C(=O)O$C_1$-$C_2$alkyl, -C(=O)Obenzyl, $C_1$-$C_3$alkoxy, phenoxy, -C(=O)-$C_1$-$C_3$alkyl or -C(=O)phenyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once or twice by halogen and/or methoxy; -C(=O)-$C_1$-$C_8$alkyl which can be unsubstituted or substituted by phenyl, -C(=O)O$C_1$-$C_2$alkyl, $C_1$-$C_3$alkoxy, phenoxy, benzyloxy or -OC(=O)-$C_1$-$C_3$alkyl; -C(=O)phenyl, where the phenyl radical can be unsubstituted or substituted once or twice by halogen, hydroxyl, methoxy, trifluoromethyl or trifluoromethoxy; -C(=O)N($C_1$-$C_2$alkyl)$_2$; -C(=S)N($C_1$-$C_2$alkyl)$_2$; -$SO_2$-$C_1$-$C_2$alkyl; -$SO_2$-benzyl or -$SO_2$-phenyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once or twice by halogen, hydroxyl, methoxy, trifluoromethyl or trifluoromethoxy; or -$SO_2$-$NR_{15}R_{16}$;
$R_2$ is $C_1$-$C_4$alkyl which can be unsubstituted or substituted by phenyl, $C_1$-$C_2$alkoxy, phenoxy or benzyloxy; -C(=O)-$C_1$-$C_4$alkyl; or a cyclic 5 to 6-membered acetal which can be unsubstituted or substituted by $C_1$-$C_4$alkyl, $C_1$-$C_4$ hydroxyalkyl, hydroxyl or benzyl

$R_3$ is hydrogen; a singly to triply charged metallic cation, or $NH_4^+$; $C_1$-$C_8$alkyl which can be unsubstituted or substituted once to three times by halogen, $C_3$-$C_6$cycloalkyl, $C_1$-$C_4$alkoxy, phenoxy, benzyloxy, hydroxyl, carboxyl, C(=O)O$C_1$-$C_4$alkyl or C(=O)Obenzyl; $C_3$-$C_6$alkenyl; $C_3$-$C_6$alkynyl; $C_3$-$C_6$cycloalkyl; phenyl, benzyl or phenethyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once to three times by halogen, $C_1$-$C_4$alkyl, hydroxyl, $C_1$-$C_2$alkoxy, trifluoromethyl or trifluoromethoxy; -C(=O)-$C_1$-$C_4$alkyl; -C(=O)phenyl; or a 5- or 6-membered heterocycle having one to three heteroatoms selected from N, O and S;
$R_4$ is hydrogen; $C_1$-$C_8$alkyl which can be unsubstituted or substituted once to three times by halogen, $C_3$-$C_6$cycloalkyl, $C_1$-$C_4$alkoxy, phenoxy, benzyloxy, hydroxyl, carboxyl, C(=O)O$C_1$-$C_4$alkyl or C(=O)Obenzyl; $C_3$-$C_6$alkenyl; $C_3$-$C_6$alkynyl; $C_3$-$C_6$cycloalkyl; phenyl, benzyl or phenethyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once to three times by halogen, $C_1$-$C_4$alkyl, hydroxyl, $C_1$-$C_2$alkoxy, trifluoromethyl or trifluoromethoxy; -C(=O)-$C_1$-$C_4$alkyl; -C(=O)phenyl; or a 5- or 6-membered heterocycle having one to three heteroatoms selected from N, O and S;
$R_5$ is hydrogen, $C_1$-$C_6$alkyl or benzyl; or
$R_4$ and $R_5$ form, together with the nitrogen atom, a cyclopentylamine, cyclohexylamine, morpholine or dimethylmorpholine ring;
$R_6$, $R_7$, $R_8$, $R_9$ and $R_{10}$ are hydrogen, $C_1$-$C_6$alkyl, phenyl or pyridyl, where the phenyl radical or pyridyl radical can be unsubstituted or substituted once to three times by halogen, $C_1$-$C_4$alkyl, hydroxyl, $C_1$-$C_2$alkoxy, trifluoromethyl or trifluoromethoxy;
n is 0 or 1; and
$R_{15}$ and $R_{16}$ are hydrogen, $C_1$-$C_4$alkyl, phenyl or benzyl.

Halogen is fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

Alkyl, on its own or as a constituent of another substituent, is to be understood as meaning straight-chain or branched-chain alkyls. Depending on the number of carbon atoms indicated, they constitute the following groups, for example: methyl, ethyl and the isomers of propyl, butyl, pentyl or hexyl, for example isopropyl, isobutyl, tert-butyl, sec-butyl or isopentyl.

Alkenyl is, for example, 1-propenyl, allyl, 1-butenyl, 2-butenyl or 3-butenyl.

Alkynyl is, for example, 1-propynyl or 1-butynyl.

Cycloalkyl is optionally cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, preferably

cyclopropyl, cyclopentyl or cyclohexyl.

Examples of those 5- or 6-membered heterocycles having nitrogen, oxygen and/or sulfur as heteroatoms which are preferred are: thiophene, thiazole, furan and pyridine.

Important compounds of the formula I are those in which $X_1$ and $X_2$ are both halogen, preferably those in which Z is -C(=O)A or -C(=S)A, in particular those in which A is hydrogen, $OR_3$, $SR_3$ or $NR_4R_5$.

Owing to their pronounced plant-protecting microbicidal properties, those active compounds of formula I are preferred which possess the following substituents or combinations of these substituents amongst themselves:

Both $X_1$ and $X_2$ are either chlorine or bromine;
Z is C(=O)A;
A is hydrogen, $OR_3$, $SR_3$ or $NHR_4$;
$R_1$ is hydrogen, acetyl or benzoyl;
$R_3$ and $R_4$ are hydrogen; $C_1$-$C_8$alkyl which can be unsubstituted or substituted once to three times by halogen, $C_3$-$C_6$cycloalkyl, $C_1$-$C_4$alkoxy, phenoxy, benzyloxy, hydroxyl, carboxyl, C(=O)O$C_1$-$C_4$alkyl or C(=O)Obenzyl; $C_3$-$C_6$alkenyl; phenyl or benzyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once to three times by halogen, hydroxyl, methoxy, trifluoromethyl and/or trifluoromethoxy; and
$R_5$ is hydrogen.

Of these, those are preferred in which
$X_1$ and $X_2$ are chlorine;
Z is COOH, $COOCH_3$ or COObenzyl; and
$R_1$ is hydrogen or acetyl.

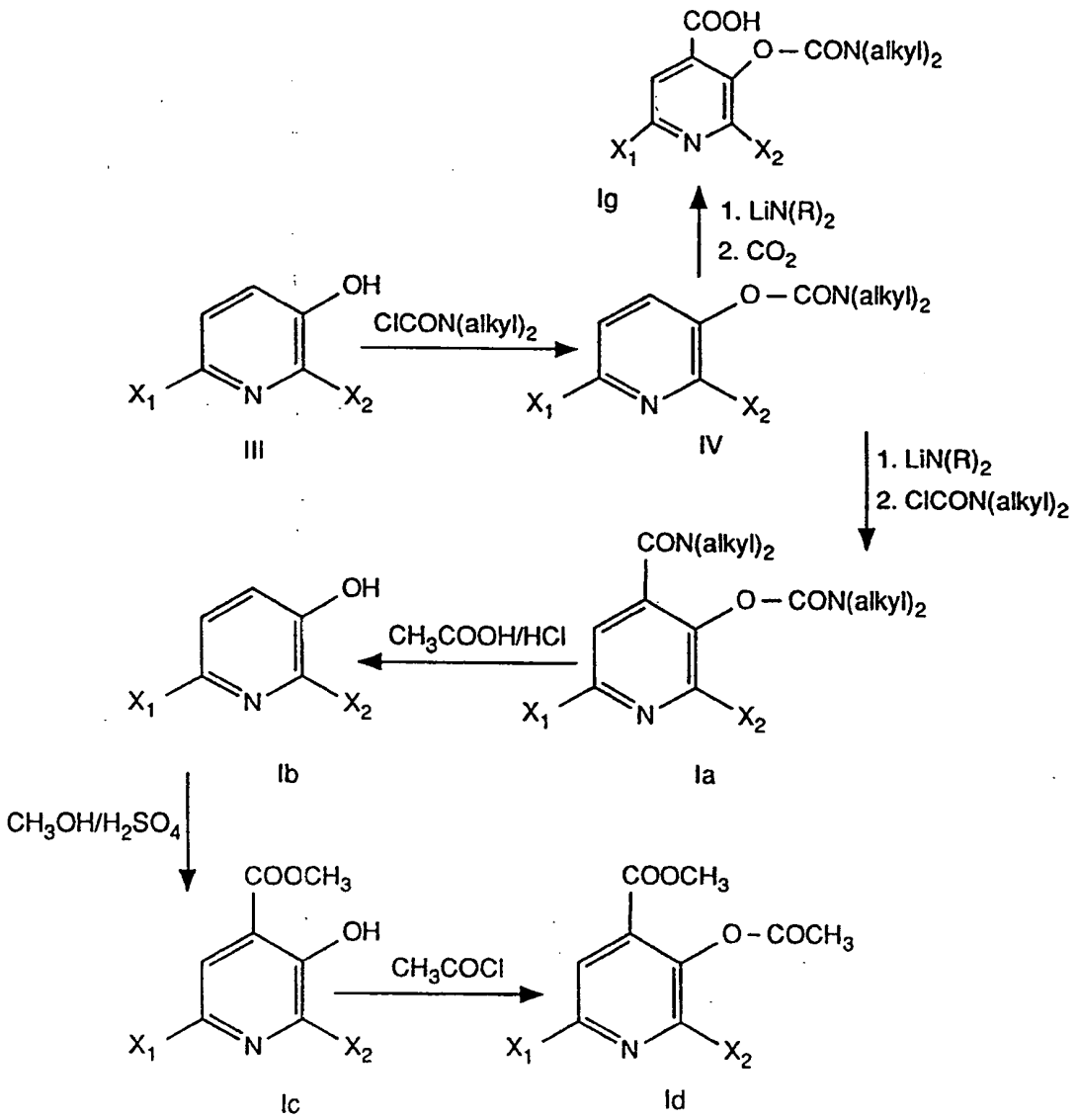
Those compounds in which Z is either -C(=O)A or -C(=S)A, and A is one of the groups $-NHOR_6$, $-ON=CR_7R_8$ or $-NH-N(=C)_n(R_9)R_{10}$ are another preferred group within the formula I.

Acetals, i.e. compounds having the structural element Z = $-CH(OR_2)_2$, are a further preferred group of the formula I. These acetals can be open acetals, which are derived from $C_1$-$C_4$alcohols which have only one OH group (e.g. methanol, ethanol, propanol,

isopropanol, etc.), or ring acetals, which are formed from $C_1$-$C_6$diols (e.g. glycol, 1,2-propanediol or 1,3-propanediol) or from glycerol.

The compounds of the formula I, in which $X_1$ is hydrogen or halogen, $X_2$ is halogen and Z is C(=O)A, and A is hydroxyl or methoxy, can be prepared as follows (Scheme 1).

Scheme 1

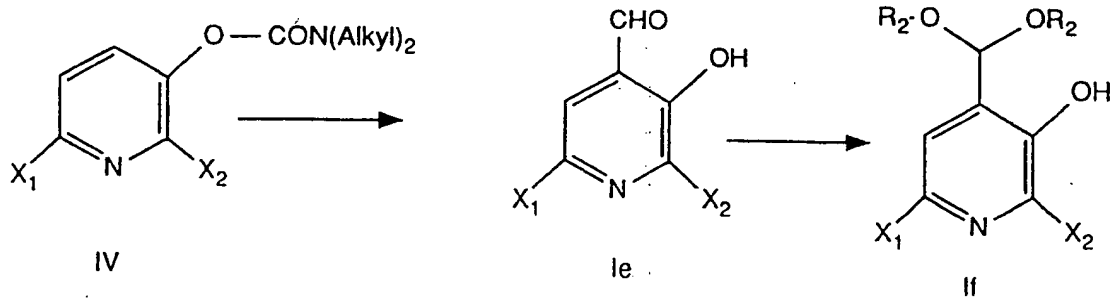



The compound of the formula III can be reacted with a N,N-dialkylchloroformamide, for example N,N-diethylchloroformamide, in a polar solvent, for example dimethylformamide

(DMF) or acetonitrile, in the presence of a base, for example triethylamine, to yield a compound of the formula IV. Metallation of a compound of the formula IV with a lithium base, for example lithium 2,2,6,6-tetramethylpiperidide (LTMP), lithium diisopropylamide (LDA) or lithium hexamethyldisilazide (LHMDS), in an aprotic solvent, for example tetrahydrofuran (THF), diethyl ether or hexane, at -20 to -80°C, and reaction with an electrophile, for example an alkyl chloroformate, a N,N-dialkylchloroformamide or $CO_2$, yields, after aqueous working-up, a compound of the formula Ia or Ig, which, by means of acidic hydrolysis, for example in a mixture of concentrated hydrochloric acid and acetic acid, react to form a compound of the formula Ib, which, by means of subsequent acid-catalysed esterification in an alcohol, for example methanol, yields a compound of the formula Ic, which, by means of reaction with a carbonyl chloride, sulfonyl chloride or alkyl halide, for example acetyl chloride, methanesulfonyl chloride, or methyl iodide, yields a compound of the formula Id or of the formula I.

The compounds of formula I, in which $X_1$ is hydrogen or halogen, $X_2$ is halogen and Z is -C(=O)A, and A and also $R_1$ are hydrogen, can be obtained in an analogous manner (Scheme 2) by metallation of a compound of the formula IV with a lithium base, for example lithium 2,2,6,6-tetramethylpiperidide, lithium diisopropylamide or lithium hexamethyldisilazide, in an aprotic solvent, for example tetrahydrofuran, diethyl ether or hexane, at -20 to -80°C, and reaction with DMF and subsequent alkaline hydrolysis, in a polar, water-miscible solvent, for example THF, with an aqueous solution of sodium or potassium hydroxide to form a compound of the formula Ie.

Scheme 2

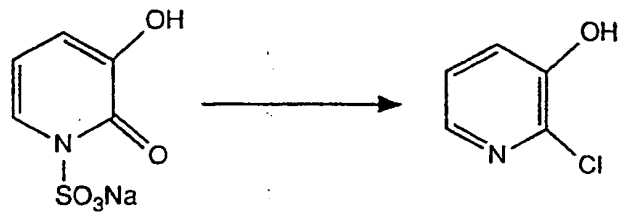



The compounds of the formula I, in which $X_1$ is hydrogen or halogen, $X_2$ is halogen and Z is $-CH(OR_2)_2$, and $R_2$ is an alkyl radical (Cmpd. If), can be prepared by reacting a compound of formula Ie with an alcohol, for example methanol or ethanol, or with a

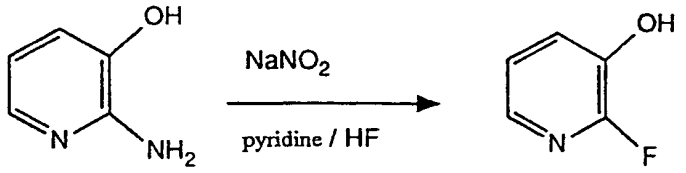
glycol, for example ethylene glycol, in a solvent, for example toluene, which can be used as an entraining agent, under acidic catalysis using, for example, p-toluenesulfonic acid, and azeotropic removal of the water of reaction.

The preparation of the intermediates of the formula III, in which $X_1$ is hydrogen and $X_2$ is F or Cl, is also the subject-matter of the invention (Scheme 3).

Scheme 3




II IIIa




IIIb

The 2-fluoro-3-pyridinol (IIIb) which is produced here is novel and can be prepared in high yield by diazotizing 2-amino-3-hydroxypyridine with sodium nitrite in a mixture of pyridine and hydrogen fluoride at temperatures of less than 25°C.

Compounds of the formula I in which $X_1 = X_2 = Cl$ can be prepared as follows: an alkali metal salt of 3-hydroxy-2-oxo-1(2H)-pyridinesulfonic acid (II), which can be prepared, for example, in accordance with Swiss Patent No. 5939 or British Patent GB-1077036, can be reacted with thionyl chloride or phosgene in an inert solvent or solvent mixture, such as DMF/toluene, at 90°C, to form 2-chloro-3-pyridinol (IIIa) in high yield (Scheme 3), which is chlorinated in DMF to form 2,6-dichloro-3-pyridinol and can subsequently be reacted with diethylcarbamoyl chloride to form 2,6-dichloro-3-N-diethylcarbamoyloxypyridine. Subsequent metallation with lithium 2,2,6,6-tetramethylpiperidide (LTMP) in THF at

-78°C and reaction with diethylcarbamoyl chloride yield N,N-diethyl-2,6-dichloro-3-(N-diethylcarbamoyloxy)isonicotinamide, which can be hydrolysed in a mixture of acetic acid and concentrated hydrochloric acid to give 2,6-dichloro-3-hydroxyisonicotinic acid, esterified in sulfuric methanol to give methyl 2,6-dichloro-3-hydroxyisonicotinate and finally reacted with acetyl chloride in a suitable solvent, for example acetonitrile, in the presence of a base such as pyridine or triethylamine to give methyl 2,6-dichloro-3-acetyloxyisonicotinate. The 2,6-dichloro-3-hydroxyisonicotinoyl chloride can be obtained by reaction of the corresponding carboxylic acid with thionyl chloride or oxalyl chloride and be reacted with nucleophiles, for example benzyl alcohol or methylamine, to give benzyl 2,6-dichloro-3-hydroxyisonicotinate or N-methyl-2,6-dichloro-3-hydroxyisonicotinamide. The corresponding thiocarboxylates or thiocarboxamides can be obtained by reaction with a thionating agent, for example phosphorus pentasulfide or 4-methoxyphenylthiophosphonic acid cyclodithioanhydride ("Lawesson reagent"), in a suitable solvent, for example toluene.

Compounds of the formula I in which $X_1 = X_2 = Br$, $R_1$ = acetyl and $Z = COOCH_3$ can be obtained by an analogous synthesis proceeding from 2,6-dibromo-3-pyridinol [Beilstein, E III/IV, Vol. 21, p. 432].

Compounds of the formula I in which $X_1 = H$ and $X_2$ = F, Cl or Br, $R_1$ = acetyl and $Z = COOCH_3$ can be obtained by an analogous synthesis proceeding from the corresponding monohalogeno-3-pyridinol.

Compounds of the formula I in which $X_1$ = Cl or Br, and $X_2$ is a halogen which is different from $X_1$, such as F, Cl or Br, $R_1$ = acetyl and $Z = COOCH_3$ can likewise be obtained by an analogous synthesis, with it being possible to obtain the 2,6-dihalides by halogenating the corresponding monohalogeno-3-pyridinols.

Suitable reaction-inert solvents and diluents are used as reaction media in process schemes 1 to 3, in conformity with the relevant reaction conditions. Examples which may be mentioned are: aliphatic and aromatic hydrocarbons, such as benzene, toluene, xylenes and petroleum ether; halogenated hydrocarbons, such as chlorobenzene, methylene chloride, ethylene chloride, chloroform, carbon tetrachloride and tetrachloroethylene; ethers and ether-like compounds, such as dialkyl ethers (diethyl ether, diisopropyl ether), tert-butyl methyl ether, etc.), anisole, dioxane and tetrahydrofuran; nitriles, such as acetonitrile and propionitrile; N,N-dialkylated amides, such as dimethylformamide;

dimethyl sulfoxide; ketones, such as acetone, diethyl ketone and methyl ethyl ketone, and mixtures of these solvents with each other.

Additional methods for preparing the precursors, also including those of the substituted 2-halopyridine derivatives, are familiar to the skilled person or are described in the specialist literature.

It has now been found, surprisingly, that, in practice, the compounds of the formula I according to the invention display a spectrum of activity which is very favourable in practice for protecting plants against diseases which are caused both by fungi and by bacteria and viruses. The underlying mode of action of the compounds according to the invention is directed, in particular, towards effecting a general increase in the resistance of the treated plants, resulting in the achievement of a general antimicrobial resistance to a broad spectrum of harmful microorganisms. The great advantage of the compounds according to the invention is that, when they are used for treating plants, they do not act directly on the phytopathogenic microorganisms but, instead, activate and stimulate the plant's own biological defence system prior to infestation, thereby providing the possibility of ensuring that the treated plants maintain their health by themselves, frequently without additional microbicidal substances being used during the vegetative period. Consequently, it is characteristic of the active compounds of the formula I that they do not exert any direct effect on the microorganisms but, instead, have the effect of immunizing healthy plants against plant diseases. The resulting immunization against plant diseases can be employed to protect a large number of crop plants so that the appearance of harmful organisms on the plants or plant parts (fruits, blossoms, foliage, stalks, tubers and roots) of different economically useful crops is efficaciously prevented, with subsequently accruing plant parts also remaining free of phytopathogenic microorganisms. However, in contrast to this, it is also possible to use a number of compounds of the formula I to protect against phytopathogenic microorganisms. The active compounds of the formula I exhibit their activity both by way of foliage application and systemically. They may also be employed as dressing agents for treating seed (fruit, tubers and grains) and plant cuttings in order to protect them against fungal infections, for example against Fusarium nivale, Helminthosporium gramineum and Ustilago nuda, and also against phytopathogenic microorganisms which occur in the soil.

The spectrum of activity of the compounds of the formula I extends, for example, to phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Colletotrichum, Helminthosporium, Fusarium, Septoria, Cercospora and

Alternaria); Basidiomycetens (e.g. the genera Hemileia, Rhizocotonia and Puccinia); Ascomycetes (e.g. Venturia, Podosphaera, Erysiphe, Monilinia and Uncinula) and the Oomycetes which belong to the Phycomycetes (e.g. Phytophthora, Plasmopara, Pythium, Bremia etc.). In addition to this, the compounds according to the invention are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp., Pseudomonas spp. and Erwinia amylovora, and also against tobacco mosaic virus).

The invention also relates to compositions which comprise the compounds of the formula I as an active compound component, in particular plant-protecting compositions, and also to their use in the agricultural sector or related areas.

In addition to this, the present invention also includes the preparation of these compositions, wherein the active substance is intimately mixed with one or more of the herein-described excipients and surfactants. The invention also includes a process for treating plants, wherein the novel compounds of the formula I, or the novel compositions containing these compounds, are applied.

The following plant species, for example, are regarded, within the scope of this invention, as being target crops for the plant-protective use which is disclosed herein: cereals (wheat, barley, rye, oats, rice, maize, sorghum and related species); beets (sugar beet and feeding beet); pip fruit, stone fruit and berry fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); legumes (beans, lentils, peas and soyabean); oil crops (rape, mustard, poppy, olives, sunflowers, coconut, castor oil, cacao and peanuts); cucumber plants (pumpkin, cucumbers and melons); fibre plants (cotton, flax, hemp and jute); citrus fruits (oranges, lemons, shaddocks and mandarins); vegetable varieties (spinach, garden lettuce, asparagus, cabbage species, carrots, onions, tomatoes, potatoes and pepper); laurel plants (avocado, cinnamon and camphor), or plants such as tobacco, nuts, coffee, sugar cane, tea, pepper, grapevines, hops, banana plants, natural rubber plants and ornamental plants (Compositae).

Active compounds of the formula I are customarily used in the form of compositions and may be added, simultaneously or successively, to the surface or plant to be treated together with additional active compounds. These additional active compounds may be either fertilizers, trace element-supplying agents or other preparations which influence plant growth. It is also possible, in this context, to use selective herbicides, such as insecticides, fungicides, bactericides, nematicides or molluscicides, or mixtures of several of these preparations, additionally, where appropriate, together with excipients, surfactants

or other administration-promoting additives which are customary in formulation technology.

Suitable excipients and additives may be solid or liquid and are those substances which are appropriate in formulation technology, for example natural or regenerated minerals, solvents, dispersants, wetting agents, adhesives, thickening agents, binding agents or fertilizers.

A preferred method for applying an active compound of the formula I or an agrochemical composition which comprises at least one of these active compounds is application to the foliage (foliage application). In this context, the frequency and rate of application depend on the infestation pressure of the pathogen concerned. However, the active compounds of the formula I can also gain entry into the plant (systemic effect) by way of the soil and through the roots, by means of the plant site being drenched with a liquid preparation or the substances being introduced into the soil in solid form, for example in the form of granules (soil application). However, the compounds of the formula I can also be applied (coating) to seed grains by either drenching the grains with a liquid preparation of the active compound or coating them with a solid preparation. In addition to this, further modes of application are possible in particular cases, for example specific treatment of the plant stems or the buds, and the treatment of rice plants by means of the so-called "into water application" or "seedling box application".

In this context, the compounds of the formula I are employed in unaltered form or, preferably, together with the adjuvants which are customary in formulation technology. For this purpose, they are expediently processed, in a known manner, for example into emulsion concentrates, spreadable pastes, directly sprayable or dilutable solutions, diluted emulsions, wettable powders, soluble powders, dusting compositions or granules, or by encapsulations in, for example, polymeric substances. The methods of application, such as spraying, nebulizing, dusting, scattering, coating or pouring, are, like the type of composition, selected in accordance with the sought-after aims and the given conditions. Advantageous rates of application are in general from 0.5 g to 5 kg of active substance (AS) per ha; preferably from 1 g to 2 kg of AS/ha, in particular from 1 g to 600 g of AS/ha and particularly preferably from 1 g to 500 g of AS/ha.

The formulations, i.e. the compositions, preparations or combinations which comprise the active compound of the formula I and, where appropriate, a solid or liquid additive, are prepared in a known manner, for example by intimately mixing and/or grinding the active

compounds with extenders, for example with solvents, solid excipients and, where appropriate, surface-active compounds (surfactants).

Suitable solvents are: aromatic hydrocarbons, preferably the $C_8$ to $C_{12}$ fractions, for example xylene mixtures or substituted naphthalenes, phthalic esters, such as dibutyl phthalate or dioctyl phthalate, aliphatic hydrocarbons, such as cyclohexane or paraffins, alcohols and glycols, and also their ethers and esters, such as ethanol, ethylene glycol, ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, ketones, such as cyclohexanone, strongly polar solvents, such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or dimethylformamide, and also, where appropriate, epoxidized plant oils such as epoxidized coconut oil or soyabean oil; or water.

As a rule, natural crushed rocks, such as calcite, talc, kaolin, montmorillonite or attapulgite, are used as solid excipients, for example for dusting compositions and dispersible powders. Highly disperse silicic acid or highly disperse, absorbent polymers can also be added in order to improve the physical properties. Porous types, for example pumice stone, crushed brick, sepiolite or bentonite, are suitable for use as granulated, adsorptive granular excipients, while calcite or sand, for example, are suitable for use as non-sorptive excipient materials. In addition to this, a large number of pregranulated materials of inorganic or organic nature can be used, such as, in particular, dolomite or comminuted plant residues. Natural (animal or vegetable) or synthetic phospholipids from the cephalins and lecithins series, which can, for example, be obtained from soyabeans, are also particularly advantageous application-promoting additives which can lead to a marked reduction in the rate of application.

Depending on the nature of the active compound of the formula I to be formulated, nonionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties are suitable for use as surface-active compounds. Surfactants are also understood to mean surfactant mixtures.

Suitable anionic surfactants can be either so-called water-soluble soaps or water-soluble, synthetic surface-active compounds.

Soaps which may be mentioned are the alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts of higher fatty acids ($C_{10}$-$C_{22}$), for example the sodium salts or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which can, for example, be obtained from coconut oil or tallow oil. In addition, the fatty

acid methyllaurine salts may also be mentioned.

However, so-called synthetic surfactants, in particular alkanesulfonates, fatty alcohol sulfonates, sulfonated benzimidazole derivatives or alkylsulfonates, are more frequently used.

Furthermore, appropriate phosphates, for example salts of the phosphoric ester of a p-nonylphenol-(4-14)-ethylene oxide adduct, also come into consideration.

Polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, saturated or unsaturated fatty acids and alkylphenols, which can contain from 3 to 30 glycol ether groups and from 8 to 20 carbon atoms in the (aliphatic) hydrocarbon residue and from 6 to 18 carbon atoms in the alkyl radical of the alkylphenols, come firstly into consideration as nonionic surfactants.

Examples of nonionic surfactants which may be mentioned are nonylphenol polyethoxy ethanols, castor oil polyglycol ethers, polypropylene-polyethylene oxide adducts, tributylphenoxypolyethylene ethanol, polyethylene glycol and octylphenoxypolyethoxy ethanol.

Furthermore, fatty acid esters of polyoxyethylenesorbitan, such as polyoxyethylene-sorbitan trioleate, also come into consideration.

The cationic surfactants are, in particular, quaternary ammonium salts which contain, as N substituents, at least one alkyl radical having from 8 to 22 C atoms, and, as additional substituents, have lower, halogenated or non-halogenated alkyl, benzyl or lower hydroxyalkyl radicals. These salts are preferably present as halides, methyl sulfates or ethyl sulfates, for example stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

Additional surfactants which are customary in formulation technology are either known to the skilled person or can be obtained from the relevant specialist literature.

As a rule, the agrochemical preparations comprise from 0.1 to 99 %, in particular from 0.1 to 95 %, of the active compound of the formula I, from 99.9 to 1 %, in particular from 99.8 to 5 %, of a solid or fluid additive, and from 0 to 25 %, in particular from 0.1 to 25 %, of a surfactant.

Whereas concentrated compositions are more likely to be preferred as a commercial product, the consumer uses diluted compositions as a rule.

The compositions may also comprise further additives, such as stabilizers, defoamers, viscosity regulators, binders, adhesives and fertilizers, or other active compounds for achieving special effects.

Agrochemical compositions which comprise compounds of the formula I as the active component likewise constitute a constituent of the present invention.

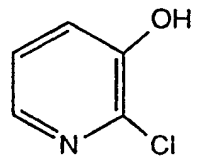
The following examples serve to explain the invention in more detail without limiting it.

1. Preparation examples

Temperatures are given in degrees centigrade.

The following abbrevations are used: Ac = acetyl, DMF = dimethylformamide; EA = ethyl acetate; Et = ethyl; sat. = saturated; i.v. = in vacuo; solv. = solvent; Me = methyl; min = minute; RM = reaction mixture; RT = room temperature; m.p. = melting point; hr = hour; THF = tetrahydrofuran; TMP = tetramethylpiperidine.

1. Preparation of 2-chloro-3-pyridinol




Process A

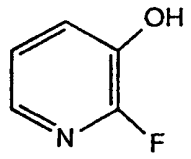
70 ml of toluene and, within the space of 15 min, a solution of 7.14 g (60 mmol) of thionyl chloride in 15 ml of toluene are added, at RT and while stirring, to a solution of 4.26 g (20 mmol) of 3-hydroxy-2-oxo-1(2H)-pyridinesulfonic acid sodium salt in 30 ml of DMF. After having been stirred at 90°C for 3 hr, the RM is cooled down to RT and poured into a mixture of 200 ml of ice water and 200 ml of EA. 150 ml of a sat. solution of sodium hydrogen carbonate are added while stirring thoroughly, and the phases are then separated; the aqueous phase is extracted once again with 100 ml of EA, and the combined organic phases are washed twice with water, dried over magnesium sulfate and concentrated i.v. at

60°C. 1.70 g are obtained of a crystalline product having an m.p. of 172°C.

Process B

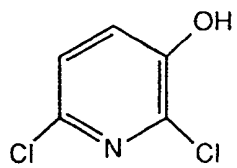
70 ml of toluene are added, while stirring, to a solution of 4.26 g (20 mmol) of 3-hydroxy-2-oxo-1(2H)-pyridinesulfonic acid sodium salt in 30 ml of DMF. While the RM is being heated to 90°C, 42.2 ml (80 mmol) of a 1.9 M solution of phosgene in toluene are added dropwise to it. After having been stirred at this temperature for 2.5 hr, the RM is cooled down to RT and poured into a mixture of 200 ml of ice water and 200 ml of EA. 250 ml of a sat. solution of sodium hydrogen carbonate are added slowly while stirring thoroughly and the phases are then separated; the aqueous phase is extracted once again with EA, and the combined organic phases are washed twice with water, dried over magnesium sulfate and concentrated i.v. at 60°C. 1.72 g are obtained of a crystalline product having an m.p. of 172°C.

2. Preparation of 2-fluoro-3-pyridinol



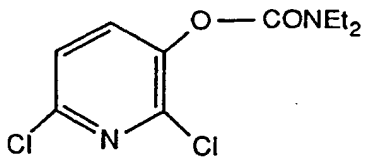

180 g of pyridine are added dropwise, in a Teflon-coated reaction vessel and at -78°C, to 400 g of hydrogen fluoride (exothermic), and 27.6 g (0.4 mol) of sodium nitrite are introduced; 40 g (0.36 mol) of 2-amino-3-pyridinol are then added over the space of 30 min after the mixture has been warmed to -20°C. After it has been warmed to RT (evolution of nitrogen), the RM is poured into ice water and this mixture is adjusted to pH 3-4 with ammonia solution and extracted four times with EA. The combined organic phases are dried over sodium sulfate and concentrated i.v. 34.5 g of yellow crystals are obtained having an m.p. of 131-132°C.

3. Preparation of 2,6-dichloro-3-pyridinol



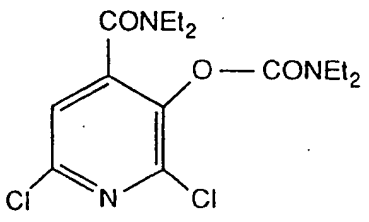
70 ml (measured at -80°C, 0.93 mol) of chlorine are passed, at 0°C and within the space of 1.5 hr, into a solution of 100 g (0.77 mol) of 2-chloro-3-pyridinol in 350 ml of DMF (exothermic). After the mixture has been allowed to stand at 20°C for 1.5 hr, the solv. is distilled off at 50°C i.v. and the residue is taken up in 100 ml of ether and 400 ml of water; the phases are separated and the aqueous phase is extracted a further five times with 100 ml of ether on each occasion. The combined organic phases are washed twice with 20 ml of water and concentrated i.v.; the residue is boiled up briefly at pH 3 in 1.6 l of water and this mixture is filtered hot, stirred up with active charcoal and filtered. After cooling and then recrystallizing from water, 33 g of white crystals are obtained having an m.p. of 136-138°C. An additional 11 g of product can be obtained by continuously extracting the mother liquor with ether.

4. Preparation of 2,6-dichloro-3-N-diethylcarbamoyloxypyridine



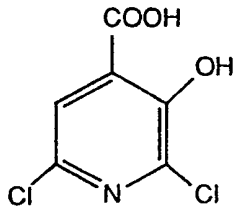

6.5 g (48 mmol) of diethylcarbamoyl chloride and 5.26 g (52 mmol) of triethylamine are added, at RT, to a solution of 7.87 g (48 mmol) of 2,6-dichloro-3-hydroxypyridine in 30 ml of acetonitrile. After having been stirred for 2 hr at reflux, the RM is poured into 200 ml of water and the whole is extracted twice with EA. The combined organic extracts are washed twice with dilute NaOH and twice with water, dried over sodium sulfate and concentrated i.v. at 60°C. Distillation on a kugelrohr at 180°C/0.1 mbar yields 10.1 g of a colourless oil.

5. Preparation of N,N-diethyl-2,6-dichloro-3-(N-diethylcarbamoyloxy)isonicotinamide



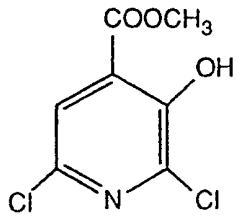
20 ml of n-butyllithium (1.6 M in hexane) are added, under nitrogen and at -20°C, to a solution of 4.66 g (33 mmol) of TMP in 50 ml of THF. After having been stirred at this temperature for 45 min, the RM is cooled down to -78°C and a solution of 6.0 g (22 mmol) of 2,6-dichloro-3-N-diethylcarbamoyloxypyridine is added within the space of 10 min. After stirring at this temperature for 45 min, 4.34 g (32 mmol) of diethylcarbamoyl chloride are added. After stirring at -78°C for 30 min, 50 ml of saturated ammonium chloride solution are added and the RM is allowed to come to RT. The mixture is extracted twice with diethyl ether, and the combined organic extracts are washed with a saturated solution of sodium chloride, dried over sodium sulfate and concentrated i.v. at 60 °C. 5.8 g of a yellow oil are obtained after chromatography through 500 g of silica gel using hexane/EA = 2:1.

6. Preparation of 2,6-dichloro-3-hydroxyisonicotinic acid




5.15 g (14.2 mmol) of N,N-diethyl-2,6-dichloro-3-(N-diethylcarbamoyloxy)isonicotinamide are boiled at reflux for 72 hr in a mixture of 50 ml of acetic acid and 100 ml of concentrated hydrochloric acid. After that, most of the acetic acid is distilled off and the remaining suspension is diluted with 200 ml of water and cooled down to 0°C; the solid is then filtered off with suction. 2.2 g of beige crystals are obtained having an m.p. of 213-215°C (decomposition).

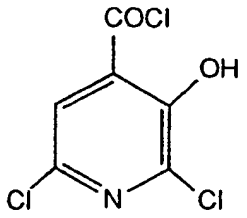
7. Preparation of methyl 2,6-dichloro-3-hydroxyisonicotinate




0.76 g (7.7 mmol) of sulfuric acid is added to a solution of 0.8 g (3.85 mmol) of 2,6-dichloro-3-hydroxyisonicotinic acid in 25 ml of methanol and this mixture is boiled at

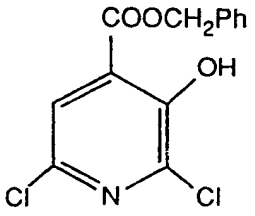
reflux for 20 hr. After adding 25 ml of methanol and 0.76 g of sulfuric acid once again, the mixture is boiled at reflux for a further 24 hr. The RM is then cooled down to RT and poured into 200 ml of water, and the whole is extracted three times with EA; the combined organic phases are washed with water, dried over sodium sulfate and concentrated i.v. at 60°C. 0.7 g of yellowish crystals having an m.p. of 88-90°C is obtained after chromatography through 20 g of silica gel using ether.

8. Preparation of 2,6-dichloro-3-hydroxyisonicotinoyl chloride



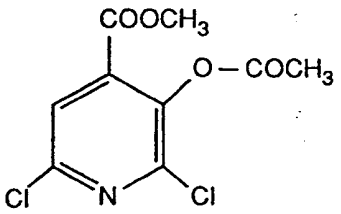

A solution of 1.5 g (7.2 mmol) of 2,6-dichloro-3-hydroxyisonicotinic acid and 5.09 g (42.8 mmol) of thionyl chloride in 35 ml of toluene is boiled at 80°C/490 mbar for 2 hr. Concentrating the RM i.v. at 60°C yields 1.6 g of brown resin.

9. Preparation of benzyl 2,6-dichloro-3-hydroxyisonicotinate



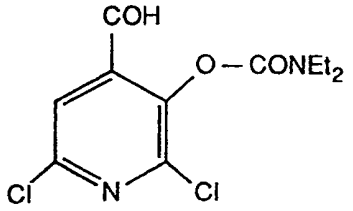

0.67 g (8.5 mmol) of pyridine is added, at RT, to a solution of 1.6 g (7 mmol) of 2,6-dichloro-3-hydroxyisonicotinoyl chloride and 0.92 g (8.5 mmol) of benzyl alcohol in 50 ml of acetonitrile. After having been stirred at RT for 3 hr, the RM is concentrated i.v. at 60°C, and the residue is taken up in EA; this solution is washed with 1 N hydrochloric acid, dried over sodium sulfate and concentrated i.v. at 60°C. Chromatography through silica gel using hexane/EA = 3:1 yields 1.2 g of a pale-brown oil.

10. Preparation of methyl 2,6-dichloro-3-acetyloxyisonicotinate



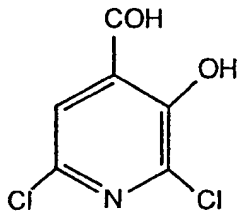

0.43 g (5.4 mmol) of pyridine is added, at RT, to a solution of 1.0 g (4.5 mmol) of methyl 2,6-dichloro-3-hydroxyisonicotinate and 0.42 g (5.4 mmol) of acetyl chloride. After having been stirred at RT for 30 min, the RM is poured into 100 ml of water and the whole is extracted with EA; the combined organic phases are washed with water, dried over sodium sulfate and concentrated i.v. at 60°C. Chromatography through 75 g of silica gel using hexane/EA yields 1.0 g of colourless crystals having an m.p. of 48-50°C.

11. Preparation of 2,6-dichloro-3-N-diethylcarbamoyloxyisonicotinaldehyde



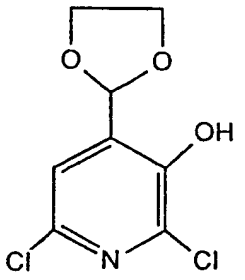

30 ml (48 mmol) of n-butyllithium (1.6 M in hexane) are added, under nitrogen and at -40°C, to a solution of 7.1 g (50 mmol) of TMP in 100 ml of THF. After stirring at this temperature for 45 min, a solution of 9.03 g (34.3 mmol) of 2,6-dichloro-3-N-diethylcarbamoyloxypyridine in 30 ml of THF is added within the space of 5 min so that the temperature does not exceed -65°C. After stirring at -78°C for 1 hr, 3.5 g (48 mmol) of DMF are added and, after the mixture has been stirred at this temperature for 20 min, the cooling bath is removed and 100 ml of a saturated solution of ammonium chloride are introduced. After that, the mixture is extracted with EA and the combined organic phases are washed twice with a saturated solution of sodium chloride, dried over sodium sulfate and concentrated i.v. at 60°C. The oily residue is stirred up with hot hexane, and this mixture is filtered and concentrated once again. 9.0 g of red oil are obtained.

12. Preparation of 2,6-dichloro-3-hydroxyisonicotinaldehyde



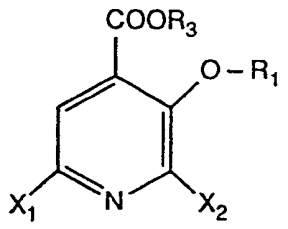

20 ml of a 1 N solution of sodium hydroxide are added, at RT and under nitrogen, to a solution of 2.85 g (9.8 mmol) of 2,6-dichloro-3-N-diethylcarbamoyloxyisonicotinaldehyde in 50 ml of THF. After 30 min, the RM is adjusted to pH 1 with 1 N hydrochloric acid and poured into 300 ml of water; this mixture is extracted twice with EA and the combined organic extracts are washed with dilute hydrochloric acid, dried over sodium sulfate and concentrated i.v. at 60°C. 2 g of red oil are obtained. Recrystallization from EA/hexane yields 0.7 g of yellowish crystals having an m.p. of 104-106°C.

13. Preparation of 2,6-dichloro-4-[1,3]dioxolan-2-ylpyridin-3-ol




A mixture of 1.5 g (7.8 mmol) of 2,6-dichloro-3-hydroxyisonicotinaldehyde and 1.3 g (21 mmol) of ethylene glycol in 100 ml of toluene is boiled on a water separator in the presence of a catalytic quantity of p-toluenesulfonic acid. After 30 min, the RM is cooled down to RT and poured into 150 ml of a dilute solution of sodium bicarbonate, with this mixture then being extracted twice with EA. The combined organic phases are washed once in each case with water and with a saturated solution of sodium chloride, dried over sodium sulfate and concentrated i.v. at 60°C. 2.45 g of a yellowish oil are obtained after chromatography on 200 ml of silica gel using a mixture of hexane/EA = 2:1.
The compounds which are listed below are obtained using the methods of preparation which have been described:

Table 1: Compounds of the formula I




| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.1 | Cl | Cl | H | H | m.p. 213-215°C |
| 1.2 | Cl | Cl | H | $COCH_3$ | m.p. 117-119°C |
| 1.3 | Cl | Cl | H | $COCH_2CH_3$ | |
| 1.4 | Cl | Cl | H | COPh | |
| 1.5 | Cl | Cl | H | $CON(Et)_2$ | oil |
| 1.6 | Cl | Cl | H | $CH_3$ | |
| 1.7 | Cl | Cl | H | $CH_2Ph$ | |
| 1.8 | Cl | Cl | $Na^+$ | H | |
| 1.9 | Cl | Cl | $Na^+$ | $COCH_3$ | |
| 1.10 | Cl | Cl | $NH_4^+$ | H | |
| 1.11 | Cl | Cl | $NH_4^+$ | $COCH_3$ | |
| 1.12 | Cl | Cl | $CH_3$ | H | m.p. 88-90°C |
| 1.13 | Cl | Cl | $CH_3$ | $COCH_3$ | m.p. 48-50°C |
| 1.14 | Cl | Cl | $CH_3$ | COPh | |
| 1.15 | Cl | Cl | $CH_2CH_3$ | H | |
| 1.16 | Cl | Cl | $CH_2CH_3$ | $COCH_3$ | |
| 1.17 | Cl | Cl | n-propyl | H | |
| 1.18 | Cl | Cl | n-propyl | $COCH_3$ | |
| 1.19 | Cl | Cl | $CH_2CH=CH_2$ | H | |
| 1.20 | Cl | Cl | $CH_2CH=CH_2$ | H | |
| 1.21 | Cl | Cl | n-butyl | H | |
| 1.22 | Cl | Cl | n-butyl | $COCH_3$ | |
| 1.23 | Cl | Cl | i-propyl | H | |
| 1.24 | Cl | Cl | i-propyl | $COCH_3$ | |
| 1.25 | Cl | Cl | i-butyl | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.26 | Cl | Cl | i-butyl | $COCH_3$ | |
| 1.27 | Cl | Cl | $CH_2$-$\Delta$ | H | |
| 1.28 | Cl | Cl | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.29 | Cl | Cl | $CH_2$phenyl | H | m.p. 71-72°C |
| 1.30 | Cl | Cl | $CH_2$phenyl | $COCH_3$ | m.p. 47-50°C |
| 1.31 | Cl | Cl | $CH_2$phenyl | COphenyl | oil |
| 1.32 | Cl | Cl | n-pentyl | H | |
| 1.33 | Cl | Cl | n-pentyl | $COCH_3$ | |
| 1.34 | Cl | Cl | cyclo$C_5H_9$ | H | |
| 1.35 | Cl | Cl | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.36 | Cl | Cl | cyc-$C_6H_{11}$ | H | |
| 1.37 | Cl | Cl | cyc-$C_6H_{11}$ | $COCH_3$ | |
| 1.38 | Cl | Cl | phenyl | H | |
| 1.39 | Cl | Cl | phenyl | $COCH_3$ | |
| 1.40 | Cl | Cl | $CH_2CF_3$ | H | |
| 1.41 | Cl | Cl | $CH_2CF_3$ | H | |
| 1.42 | Cl | Cl | $CH_2CH_2OCH_3$ | H | |
| 1.43 | Cl | Cl | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.44 | Cl | Cl | $CH_2CH_2O$phenyl | H | |
| 1.45 | Cl | Cl | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.46 | Cl | Cl | 2-F-benzyl | H | |
| 1.47 | Cl | Cl | 2-F-benzyl | $COCH_3$ | |
| 1.48 | Cl | Cl | 3-F-benzyl | H | |
| 1.49 | Cl | Cl | 3-F-benzyl | $COCH_3$ | |
| 1.50 | Cl | Cl | 4-F-benzyl | H | |
| 1.51 | Cl | Cl | 4-F-benzyl | $COCH_3$ | |
| 1.52 | Cl | Cl | 2-MeO-benzyl | H | |
| 1.53 | Cl | Cl | 2-MeO-benzyl | $COCH_3$ | |
| 1.54 | Cl | Cl | 4-MeO-benzyl | H | |
| 1.55 | Cl | Cl | 4-MeO-benzyl | $COCH_3$ | |
| 1.56 | Cl | Cl | $CH_2$-2-pyridyl | H | |
| 1.57 | Cl | Cl | $CH_2$-2-pyridyl | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.58 | Cl | Cl | $CH_2$-3-pyridyl | H | |
| 1.59 | Cl | Cl | $CH_2$-3-pyridyl | $COCH_3$ | |
| 1.60 | Cl | Cl | $CH_2$-4-pyridyl | H | |
| 1.61 | Cl | Cl | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.62 | Cl | Cl | N=CH($CH_3$)phenyl | H | |
| 1.63 | Cl | Cl | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.64 | Cl | Cl | N=CH($CH_3$)-4Clphenyl | H | |
| 1.65 | Cl | Cl | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.66 | Cl | Cl | $CH_2$-2-furanyl | H | |
| 1.67 | Cl | Cl | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.68 | Cl | Cl | $CH_2$-2-thienyl | H | |
| 1.69 | Cl | Cl | $CH_2$-2-thienyl | $COCH_3$ | |
| 1.70 | Br | Cl | H | H | |
| 1.71 | Br | Cl | H | $COCH_3$ | |
| 1.72 | Br | Cl | H | $COCH_2CH_3$ | |
| 1.73 | Br | Cl | H | COPh | |
| 1.74 | Br | Cl | H | $CON(Et)_2$ | |
| 1.75 | Br | Cl | H | $CH_3$ | |
| 1.76 | Br | Cl | H | $CH_2Ph$ | |
| 1.77 | Br | Cl | $Na^+$ | H | |
| 1.78 | Br | Cl | $Na^+$ | $COCH_3$ | |
| 1.79 | Br | Cl | $NH_4^+$ | H | |
| 1.80 | Br | Cl | $NH_4^+$ | $COCH_3$ | |
| 1.81 | Br | Cl | $CH_3$ | H | |
| 1.82 | Br | Cl | $CH_3$ | $COCH_3$ | |
| 1.83 | Br | Cl | $CH_3$ | COPh | |
| 1.84 | Br | Cl | $CH_2CH_3$ | H | |
| 1.85 | Br | Cl | $CH_2CH_3$ | $COCH_3$ | |
| 1.86 | Br | Cl | n-propyl | H | |
| 1.87 | Br | Cl | n-propyl | $COCH_3$ | |
| 1.88 | Br | Cl | $CH_2CH=CH_2$ | H | |
| 1.89 | Br | Cl | $CH_2CH=CH_2$ | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.90 | Br | Cl | n-butyl | H | |
| 1.91 | Br | Cl | n-butyl | $COCH_3$ | |
| 1.92 | Br | Cl | i-propyl | H | |
| 1.93 | Br | Cl | i-propyl | $COCH_3$ | |
| 1.94 | Br | Cl | i-butyl | H | |
| 1.95 | Br | Cl | i-butyl | $COCH_3$ | |
| 1.96 | Br | Cl | $CH_2$-$\Delta$ | H | |
| 1.97 | Br | Cl | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.98 | Br | Cl | $CH_2$phenyl | H | |
| 1.99 | Br | Cl | $CH_2$phenyl | $COCH_3$ | |
| 1.100 | Br | Cl | $CH_2$phenyl | COphenyl | |
| 1.101 | Br | Cl | n-pentyl | H | |
| 1.102 | Br | Cl | n-pentyl | $COCH_3$ | |
| 1.103 | Br | Cl | cyclo$C_5H_9$ | H | |
| 1.104 | Br | Cl | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.105 | Br | Cl | cyc-$C_6H_{11}$ | H | |
| 1.106 | Br | Cl | cyc-$C_6H_{11}$ | $COCH_3$ | |
| 1.107 | Br | Cl | phenyl | H | |
| 1.108 | Br | Cl | phenyl | $COCH_3$ | |
| 1.109 | Br | Cl | $CH_2CF_3$ | H | |
| 1.110 | Br | Cl | $CH_2CF_3$ | H | |
| 1.111 | Br | Cl | $CH_2CH_2OCH_3$ | H | |
| 1.112 | Br | Cl | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.113 | Br | Cl | $CH_2CH_2O$phenyl | H | |
| 1.114 | Br | Cl | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.115 | Br | Cl | 2-F-benzyl | H | |
| 1.116 | Br | Cl | 2-F-benzyl | $COCH_3$ | |
| 1.117 | Br | Cl | 3-F-benzyl | H | |
| 1.118 | Br | Cl | 3-F-benzyl | $COCH_3$ | |
| 1.119 | Br | Cl | 4-F-benzyl | H | |
| 1.120 | Br | Cl | 4-F-benzyl | $COCH_3$ | |
| 1.121 | Br | Cl | 2-MeO-benzyl | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.122 | Br | Cl | 2-MeO-benzyl | $COCH_3$ | |
| 1.123 | Br | Cl | 4-MeO-benzyl | H | |
| 1.124 | Br | Cl | 4-MeO-benzyl | $COCH_3$ | |
| 1.125 | Br | Cl | $CH_2$-2-pyridyl | H | |
| 1.126 | Br | Cl | $CH_2$-2-pyridyl | $COCH_3$ | |
| 1.127 | Br | Cl | $CH_2$-3-pyridyl | H | |
| 1.128 | Br | Cl | $CH_2$-3-pyridyl | $COCH_3$ | |
| 1.129 | Br | Cl | $CH_2$-4-pyridyl | H | |
| 1.130 | Br | Cl | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.131 | Br | Cl | N=CH($CH_3$)phenyl | H | |
| 1.132 | Br | Cl | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.133 | Br | Cl | N=CH($CH_3$)-4Clphenyl | H | |
| 1.134 | Br | Cl | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.135 | Br | Cl | $CH_2$-2-furanyl | H | |
| 1.136 | Br | Cl | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.137 | Br | Cl | $CH_2$-2-thienyl | H | |
| 1.138 | Br | Cl | $CH_2$-2-thienyl | $COCH_3$ | |
| 1.139 | Cl | Br | H | H | |
| 1.140 | Cl | Br | H | $COCH_3$ | |
| 1.141 | Cl | Br | H | $COCH_2CH_3$ | |
| 1.142 | Cl | Br | H | COPh | |
| 1.143 | Cl | Br | H | $CON(Et)_2$ | |
| 1.144 | Cl | Br | H | $CH_3$ | |
| 1.145 | Cl | Br | H | $CH_2Ph$ | |
| 1.146 | Cl | Br | $Na^+$ | H | |
| 1.147 | Cl | Br | $Na^+$ | $COCH_3$ | |
| 1.148 | Cl | Br | $NH_4^+$ | H | |
| 1.149 | Cl | Br | $NH_4^+$ | $COCH_3$ | |
| 1.150 | Cl | Br | $CH_3$ | H | |
| 1.151 | Cl | Br | $CH_3$ | $COCH_3$ | |
| 1.152 | Cl | Br | $CH_3$ | COPh | |
| 1.153 | Cl | Br | $CH_2CH_3$ | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.154 | Cl | Br | $CH_2CH_3$ | $COCH_3$ | |
| 1.155 | Cl | Br | n-propyl | H | |
| 1.156 | Cl | Br | n-propyl | $COCH_3$ | |
| 1.157 | Cl | Br | $CH_2CH=CH_2$ | H | |
| 1.158 | Cl | Br | $CH_2CH=CH_2$ | H | |
| 1.159 | Cl | Br | n-butyl | H | |
| 1.160 | Cl | Br | n-butyl | $COCH_3$ | |
| 1.161 | Cl | Br | i-propyl | H | |
| 1.162 | Cl | Br | i-propyl | $COCH_3$ | |
| 1.163 | Cl | Br | i-butyl | H | |
| 1.164 | Cl | Br | i-butyl | $COCH_3$ | |
| 1.165 | Cl | Br | $CH_2$-$\Delta$ | H | |
| 1.166 | Cl | Br | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.167 | Cl | Br | $CH_2$phenyl | H | |
| 1.168 | Cl | Br | $CH_2$phenyl | $COCH_3$ | |
| 1.169 | Cl | Br | $CH_2$phenyl | COphenyl | |
| 1.170 | Cl | Br | n-pentyl | H | |
| 1.171 | Cl | Br | n-pentyl | $COCH_3$ | |
| 1.172 | Cl | Br | cyclo$C_5H_9$ | H | |
| 1.173 | Cl | Br | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.174 | Cl | Br | cyc-$C_6H_{11}$ | H | |
| 1.175 | Cl | Br | cyc-$C_6H_{11}$ | $COCH_3$ | |
| 1.176 | Cl | Br | phenyl | H | |
| 1.177 | Cl | Br | phenyl | $COCH_3$ | |
| 1.178 | Cl | Br | $CH_2CF_3$ | H | |
| 1.179 | Cl | Br | $CH_2CF_3$ | H | |
| 1.180 | Cl | Br | $CH_2CH_2OCH_3$ | H | |
| 1.181 | Cl | Br | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.182 | Cl | Br | $CH_2CH_2O$phenyl | H | |
| 1.183 | Cl | Br | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.184 | Cl | Br | 2-F-benzyl | H | |
| 1.185 | Cl | Br | 2-F-benzyl | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.186 | Cl | Br | 3-F-benzyl | H | |
| 1.187 | Cl | Br | 3-F-benzyl | $COCH_3$ | |
| 1.188 | Cl | Br | 4-F-benzyl | H | |
| 1.189 | Cl | Br | 4-F-benzyl | $COCH_3$ | |
| 1.190 | Cl | Br | 2-MeO-benzyl | H | |
| 1.191 | Cl | Br | 2-MeO-benzyl | $COCH_3$ | |
| 1.192 | Cl | Br | 4-MeO-benzyl | H | |
| 1.193 | Cl | Br | 4-MeO-benzyl | $COCH_3$ | |
| 1.194 | Cl | Br | $CH_2$-2-pyridyl | H | |
| 1.195 | Cl | Br | $CH_2$-2-pyridyl | $COCH_3$ | |
| 1.196 | Cl | Br | $CH_2$-3-pyridyl | H | |
| 1.197 | Cl | Br | $CH_2$-3-pyridyl | $COCH_3$ | |
| 1.198 | Cl | Br | $CH_2$-4-pyridyl | H | |
| 1.199 | Cl | Br | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.200 | Cl | Br | N=CH($CH_3$)phenyl | H | |
| 1.201 | Cl | Br | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.202 | Cl | Br | N=CH($CH_3$)-4Clphenyl | H | |
| 1.203 | Cl | Br | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.204 | Cl | Br | $CH_2$-2-furanyl | H | |
| 1.205 | Cl | Br | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.206 | Cl | Br | $CH_2$-2-thienyl | H | |
| 1.207 | Cl | Br | $CH_2$-2-thienyl | $COCH_3$ | |
| 1.208 | Cl | F | H | H | |
| 1.209 | Cl | F | H | $COCH_3$ | |
| 1.210 | Cl | F | H | $COCH_2CH_3$ | |
| 1.211 | Cl | F | H | COPh | |
| 1.212 | Cl | F | H | $CON(Et)_2$ | |
| 1.213 | Cl | F | H | $CH_3$ | |
| 1.214 | Cl | F | H | $CH_2Ph$ | |
| 1.215 | Cl | F | $Na^+$ | H | |
| 1.216 | Cl | F | $Na^+$ | $COCH_3$ | |
| 1.217 | Cl | F | $NH_4^+$ | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.218 | Cl | F | $NH_4^+$ | $COCH_3$ | |
| 1.219 | Cl | F | $CH_3$ | H | |
| 1.220 | Cl | F | $CH_3$ | $COCH_3$ | |
| 1.221 | Cl | F | $CH_3$ | COPh | |
| 1.222 | Cl | F | $CH_2CH_3$ | H | |
| 1.223 | Cl | F | $CH_2CH_3$ | $COCH_3$ | |
| 1.224 | Cl | F | n-propyl | H | |
| 1.225 | Cl | F | n-propyl | $COCH_3$ | |
| 1.226 | Cl | F | $CH_2CH=CH_2$ | H | |
| 1.227 | Cl | F | $CH_2CH=CH_2$ | H | |
| 1.228 | Cl | F | n-butyl | H | |
| 1.229 | Cl | F | n-butyl | $COCH_3$ | |
| 1.230 | Cl | F | i-propyl | H | |
| 1.231 | Cl | F | i-propyl | $COCH_3$ | |
| 1.232 | Cl | F | i-butyl | H | |
| 1.233 | Cl | F | i-butyl | $COCH_3$ | |
| 1.234 | Cl | F | $CH_2$-$\Delta$ | H | |
| 1.235 | Cl | F | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.236 | Cl | F | $CH_2$phenyl | H | |
| 1.237 | Cl | F | $CH_2$phenyl | $COCH_3$ | |
| 1.238 | Cl | F | $CH_2$phenyl | COphenyl | |
| 1.239 | Cl | F | n-pentyl | H | |
| 1.240 | Cl | F | n-pentyl | $COCH_3$ | |
| 1.241 | Cl | F | cyclo$C_5H_9$ | H | |
| 1.242 | Cl | F | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.243 | Cl | F | cyc-$C_6H_{11}$ | H | |
| 1.244 | Cl | F | cyc-$C_6H_{11}$ | $COCH_3$ | |
| 1.245 | Cl | F | phenyl | H | |
| 1.246 | Cl | F | phenyl | $COCH_3$ | |
| 1.247 | Cl | F | $CH_2CF_3$ | H | |
| 1.248 | Cl | F | $CH_2CF_3$ | H | |
| 1.249 | Cl | F | $CH_2CH_2OCH_3$ | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.250 | Cl | F | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.251 | Cl | F | $CH_2CH_2O$phenyl | H | |
| 1.252 | Cl | F | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.253 | Cl | F | 2-F-benzyl | H | |
| 1.254 | Cl | F | 2-F-benzyl | $COCH_3$ | |
| 1.255 | Cl | F | 3-F-benzyl | H | |
| 1.256 | Cl | F | 3-F-benzyl | $COCH_3$ | |
| 1.257 | Cl | F | 4-F-benzyl | H | |
| 1.258 | Cl | F | 4-F-benzyl | $COCH_3$ | |
| 1.259 | Cl | F | 2-MeO-benzyl | H | |
| 1.260 | Cl | F | 2-MeO-benzyl | $COCH_3$ | |
| 1.261 | Cl | F | 4-MeO-benzyl | H | |
| 1.262 | Cl | F | 4-MeO-benzyl | $COCH_3$ | |
| 1.263 | Cl | F | $CH_2$-2-pyridyl | H | |
| 1.264 | Cl | F | $CH_2$-2-pyridyl | $COCH_3$ | |
| 1.265 | Cl | F | $CH_2$-3-pyridyl | H | |
| 1.266 | Cl | F | $CH_2$-3-pyridyl | $COCH_3$ | |
| 1.267 | Cl | F | $CH_2$-4-pyridyl | H | |
| 1.268 | Cl | F | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.269 | Cl | F | N=CH($CH_3$)phenyl | H | |
| 1.270 | Cl | F | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.271 | Cl | F | N=CH($CH_3$)-4Clphenyl | H | |
| 1.272 | Cl | F | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.273 | Cl | F | $CH_2$-2-furanyl | H | |
| 1.274 | Cl | F | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.275 | Cl | F | $CH_2$-2-thienyl | H | |
| 1.276 | Cl | F | $CH_2$-2-thienyl | $COCH_3$ | |
| 1.277 | H | Cl | H | H | m.p. 250-253°C |
| 1.278 | H | Cl | H | $COCH_3$ | |
| 1.279 | H | Cl | H | $COCH_2CH_3$ | |
| 1.280 | H | Cl | H | COPh | |
| 1.281 | H | Cl | H | $CON(Et)_2$ | m.p. 152-153°C |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.282 | H | Cl | H | $CH_3$ | |
| 1.283 | H | Cl | H | $CH_2Ph$ | |
| 1.284 | H | Cl | $Na^+$ | H | |
| 1.285 | H | Cl | $Na^+$ | $COCH_3$ | |
| 1.286 | H | Cl | $NH_4^+$ | H | |
| 1.287 | H | Cl | $NH_4^+$ | $COCH_3$ | |
| 1.288 | H | Cl | $CH_3$ | H | m.p. 74°C |
| 1.289 | H | Cl | $CH_3$ | $COCH_3$ | |
| 1.290 | H | Cl | $CH_3$ | COPh | |
| 1.291 | H | Cl | $CH_2CH_3$ | H | |
| 1.292 | H | Cl | $CH_2CH_3$ | $COCH_3$ | |
| 1.293 | H | Cl | n-propyl | H | |
| 1.294 | H | Cl | n-propyl | $COCH_3$ | |
| 1.295 | H | Cl | $CH_2CH=CH_2$ | H | |
| 1.296 | H | Cl | $CH_2CH=CH_2$ | H | |
| 1.297 | H | Cl | n-butyl | H | |
| 1.298 | H | Cl | n-butyl | $COCH_3$ | |
| 1.299 | H | Cl | i-propyl | H | |
| 1.300 | H | Cl | i-propyl | $COCH_3$ | |
| 1.301 | H | Cl | i-butyl | H | |
| 1.302 | H | Cl | i-butyl | $COCH_3$ | |
| 1.303 | H | Cl | $CH_2$-$\Delta$ | H | |
| 1.304 | H | Cl | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.305 | H | Cl | $CH_2$phenyl | H | |
| 1.306 | H | Cl | $CH_2$phenyl | $COCH_3$ | |
| 1.307 | H | Cl | $CH_2$phenyl | COphenyl | |
| 1.308 | H | Cl | n-pentyl | H | |
| 1.309 | H | Cl | n-pentyl | $COCH_3$ | |
| 1.310 | H | Cl | cyclo$C_5H_9$ | H | |
| 1.311 | H | Cl | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.312 | H | Cl | cyc-$C_6H_{11}$ | H | |
| 1.313 | H | Cl | cyc-$C_6H_{11}$ | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.314 | H | Cl | phenyl | H | |
| 1.315 | H | Cl | phenyl | $COCH_3$ | |
| 1.316 | H | Cl | $CH_2CF_3$ | H | |
| 1.317 | H | Cl | $CH_2CF_3$ | H | |
| 1.318 | H | Cl | $CH_2CH_2OCH_3$ | H | |
| 1.319 | H | Cl | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.320 | H | Cl | $CH_2CH_2O$phenyl | H | |
| 1.321 | H | Cl | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.322 | H | Cl | 2-F-benzyl | H | |
| 1.323 | H | Cl | 2-F-benzyl | $COCH_3$ | |
| 1.324 | H | Cl | 3-F-benzyl | H | |
| 1.325 | H | Cl | 3-F-benzyl | $COCH_3$ | |
| 1.326 | H | Cl | 4-F-benzyl | H | |
| 1.327 | H | Cl | 4-F-benzyl | $COCH_3$ | |
| 1.328 | H | Cl | 2-MeO-benzyl | H | |
| 1.329 | H | Cl | 2-MeO-benzyl | $COCH_3$ | |
| 1.330 | H | Cl | 4-MeO-benzyl | H | |
| 1.331 | H | Cl | 4-MeO-benzyl | $COCH_3$ | |
| 1.332 | H | Cl | $CH_2$-2-pyridyl | H | |
| 1.333 | H | Cl | $CH_2$-2-pyridyl | $COCH_3$ | |
| 1.334 | H | Cl | $CH_2$-3-pyridyl | H | |
| 1.335 | H | Cl | $CH_2$-3-pyridyl | $COCH_3$ | |
| 1.336 | H | Cl | $CH_2$-4-pyridyl | H | |
| 1.337 | H | Cl | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.338 | H | Cl | N=CH($CH_3$)phenyl | H | |
| 1.339 | H | Cl | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.340 | H | Cl | N=CH($CH_3$)-4Clphenyl | H | |
| 1.341 | H | Cl | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.342 | H | Cl | $CH_2$-2-furanyl | H | |
| 1.343 | H | Cl | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.344 | H | Cl | $CH_2$-2-thienyl | H | |
| 1.345 | H | Cl | $CH_2$-2-thienyl | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.346 | Br | F | H | H | |
| 1.347 | Br | F | H | $COCH_3$ | |
| 1.348 | Br | F | H | $COCH_2CH_3$ | |
| 1.349 | Br | F | H | COPh | |
| 1.350 | Br | F | H | $CON(Et)_2$ | |
| 1.351 | Br | F | H | $CH_3$ | |
| 1.352 | Br | F | H | $CH_2Ph$ | |
| 1.353 | Br | F | $Na^+$ | H | |
| 1.354 | Br | F | $Na^+$ | $COCH_3$ | |
| 1.355 | Br | F | $NH_4^+$ | H | |
| 1.356 | Br | F | $NH_4^+$ | $COCH_3$ | |
| 1.357 | Br | F | $CH_3$ | H | |
| 1.358 | Br | F | $CH_3$ | $COCH_3$ | |
| 1.359 | Br | F | $CH_3$ | COPh | |
| 1.360 | Br | F | $CH_2CH_3$ | H | |
| 1.361 | Br | F | $CH_2CH_3$ | $COCH_3$ | |
| 1.362 | Br | F | n-propyl | H | |
| 1.363 | Br | F | n-propyl | $COCH_3$ | |
| 1.364 | Br | F | $CH_2CH=CH_2$ | H | |
| 1.365 | Br | F | $CH_2CH=CH_2$ | H | |
| 1.366 | Br | F | n-butyl | H | |
| 1.367 | Br | F | n-butyl | $COCH_3$ | |
| 1.368 | Br | F | i-propyl | H | |
| 1.370 | Br | F | i-propyl | $COCH_3$ | |
| 1.371 | Br | F | i-butyl | H | |
| 1.372 | Br | F | i-butyl | $COCH_3$ | |
| 1.373 | Br | F | $CH_2$-$\Delta$ | H | |
| 1.374 | Br | F | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.375 | Br | F | $CH_2$phenyl | H | |
| 1.376 | Br | F | $CH_2$phenyl | $COCH_3$ | |
| 1.377 | Br | F | $CH_2$phenyl | COphenyl | |
| 1.378 | Br | F | n-pentyl | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.379 | Br | F | n-pentyl | $COCH_3$ | |
| 1.380 | Br | F | cyclo$C_5H_9$ | H | |
| 1.381 | Br | F | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.382 | Br | F | cyc-$C_6H_{11}$ | H | |
| 1.383 | Br | F | cyc-$C_6H_{11}$ | $COCH_3$ | |
| 1.384 | Br | F | phenyl | H | |
| 1.385 | Br | F | phenyl | $COCH_3$ | |
| 1.386 | Br | F | $CH_2CF_3$ | H | |
| 1.387 | Br | F | $CH_2CF_3$ | H | |
| 1.388 | Br | F | $CH_2CH_2OCH_3$ | H | |
| 1.389 | Br | F | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.390 | Br | F | $CH_2CH_2O$phenyl | H | |
| 1.391 | Br | F | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.392 | Br | F | 2-F-benzyl | H | |
| 1.393 | Br | F | 2-F-benzyl | $COCH_3$ | |
| 1.394 | Br | F | 3-F-benzyl | H | |
| 1.395 | Br | F | 3-F-benzyl | $COCH_3$ | |
| 1.396 | Br | F | 4-F-benzyl | H | |
| 1.397 | Br | F | 4-F-benzyl | $COCH_3$ | |
| 1.398 | Br | F | 2-MeO-benzyl | H | |
| 1.399 | Br | F | 2-MeO-benzyl | $COCH_3$ | |
| 1.400 | Br | F | 4-MeO-benzyl | H | |
| 1.401 | Br | F | 4-MeO-benzyl | $COCH_3$ | |
| 1.402 | Br | F | $CH_2$-2-pyridyl | H | |
| 1.403 | Br | F | $CH_2$-2-pyridyl | $COCH_3$ | |
| 1.404 | Br | F | $CH_2$-3-pyridyl | H | |
| 1.405 | Br | F | $CH_2$-3-pyridyl | $COCH_3$ | |
| 1.406 | Br | F | $CH_2$-4-pyridyl | H | |
| 1.407 | Br | F | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.408 | Br | F | N=CH($CH_3$)phenyl | H | |
| 1.409 | Br | F | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.410 | Br | F | N=CH($CH_3$)-4Clphenyl | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.411 | Br | F | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.412 | Br | F | $CH_2$-2-furanyl | H | |
| 1.413 | Br | F | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.414 | Br | F | $CH_2$-2-thienyl | H | |
| 1.415 | Br | F | $CH_2$-2-thienyl | $COCH_3$ | |
| 1.416 | Br | Br | H | H | m.p. 207-209°C |
| 1.417 | Br | Br | H | $COCH_3$ | |
| 1.418 | Br | Br | H | $COCH_2CH_3$ | |
| 1.419 | Br | Br | H | COPh | |
| 1.420 | Br | Br | H | $CON(Et)_2$ | |
| 1.421 | Br | Br | H | $CH_3$ | |
| 1.422 | Br | Br | H | $CH_2Ph$ | |
| 1.423 | Br | Br | $Na^+$ | H | |
| 1.424 | Br | Br | $Na^+$ | $COCH_3$ | |
| 1.425 | Br | Br | $NH_4^+$ | H | |
| 1.426 | Br | Br | $NH_4^+$ | $COCH_3$ | m.p. 116-118°C |
| 1.427 | Br | Br | $CH_3$ | H | m.p. 71-73°C |
| 1.428 | Br | Br | $CH_3$ | $COCH_3$ | |
| 1.429 | Br | Br | $CH_3$ | COPh | |
| 1.430 | Br | Br | $CH_2CH_3$ | H | |
| 1.431 | Br | Br | $CH_2CH_3$ | $COCH_3$ | |
| 1.432 | Br | Br | n-propyl | H | |
| 1.433 | Br | Br | n-propyl | $COCH_3$ | |
| 1.434 | Br | Br | $CH_2CH=CH_2$ | H | |
| 1.435 | Br | Br | $CH_2CH=CH_2$ | H | |
| 1.436 | Br | Br | n-butyl | H | |
| 1.437 | Br | Br | n-butyl | $COCH_3$ | |
| 1.438 | Br | Br | i-propyl | H | |
| 1.439 | Br | Br | i-propyl | $COCH_3$ | |
| 1.440 | Br | Br | i-butyl | H | |
| 1.441 | Br | Br | i-butyl | $COCH_3$ | |
| 1.442 | Br | Br | $CH_2$-$\Delta$ | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.443 | Br | Br | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.444 | Br | Br | $CH_2$phenyl | H | |
| 1.445 | Br | Br | $CH_2$phenyl | $COCH_3$ | |
| 1.446 | Br | Br | $CH_2$phenyl | COphenyl | |
| 1.447 | Br | Br | n-pentyl | H | |
| 1.448 | Br | Br | n-pentyl | $COCH_3$ | |
| 1.449 | Br | Br | cyclo$C_5H_9$ | H | |
| 1.450 | Br | Br | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.451 | Br | Br | cyc-$C_6H_{11}$ | H | |
| 1.452 | Br | Br | cyc-$C_6H_{11}$ | $COCH_3$ | |
| 1.453 | Br | Br | phenyl | H | |
| 1.454 | Br | Br | phenyl | $COCH_3$ | |
| 1.455 | Br | Br | $CH_2CF_3$ | H | |
| 1.456 | Br | Br | $CH_2CF_3$ | H | |
| 1.457 | Br | Br | $CH_2CH_2OCH_3$ | H | |
| 1.458 | Br | Br | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.459 | Br | Br | $CH_2CH_2O$phenyl | H | |
| 1.460 | Br | Br | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.461 | Br | Br | 2-F-benzyl | H | |
| 1.462 | Br | Br | 2-F-benzyl | $COCH_3$ | |
| 1.463 | Br | Br | 3-F-benzyl | H | |
| 1.464 | Br | Br | 3-F-benzyl | $COCH_3$ | |
| 1.465 | Br | Br | 4-F-benzyl | H | |
| 1.466 | Br | Br | 4-F-benzyl | $COCH_3$ | |
| 1.467 | Br | Br | 2-MeO-benzyl | H | |
| 1.468 | Br | Br | 2-MeO-benzyl | $COCH_3$ | |
| 1.469 | Br | Br | 4-MeO-benzyl | H | |
| 1.470 | Br | Br | 4-MeO-benzyl | $COCH_3$ | |
| 1.471 | Br | Br | $CH_2$-2-pyridyl | H | |
| 1.472 | Br | Br | $CH_2$-2-pyridyl | $COCH_3$ | |
| 1.473 | Br | Br | $CH_2$-3-pyridyl | H | |
| 1.474 | Br | Br | $CH_2$-3-pyridyl | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.475 | Br | Br | $CH_2$-4-pyridyl | H | |
| 1.476 | Br | Br | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.477 | Br | Br | N=CH($CH_3$)phenyl | H | |
| 1.478 | Br | Br | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.479 | Br | Br | N=CH($CH_3$)-4Clphenyl | H | |
| 1.480 | Br | Br | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.841 | Br | Br | $CH_2$-2-furanyl | H | |
| 1.482 | Br | Br | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.483 | Br | Br | $CH_2$-2-thienyl | H | |
| 1.484 | Br | Br | $CH_2$-2-thienyl | $COCH_3$ | |
| 1.485 | H | F | H | H | |
| 1.486 | H | F | H | $COCH_3$ | |
| 1.487 | H | F | H | $COCH_2CH_3$ | |
| 1.488 | H | F | H | COPh | |
| 1.489 | H | F | H | $CON(Et)_2$ | |
| 1.490 | H | F | H | $CH_3$ | |
| 1.491 | H | F | H | $CH_2Ph$ | |
| 1.492 | H | F | $Na^+$ | H | |
| 1.493 | H | F | $Na^+$ | $COCH_3$ | |
| 1.494 | H | F | $NH_4^+$ | H | |
| 1.495 | H | F | $NH_4^+$ | $COCH_3$ | |
| 1.496 | H | F | $CH_3$ | H | |
| 1.497 | H | F | $CH_3$ | $COCH_3$ | |
| 1.498 | H | F | $CH_3$ | COPh | |
| 1.499 | H | F | $CH_2CH_3$ | H | |
| 1.500 | H | F | $CH_2CH_3$ | $COCH_3$ | |
| 1.501 | H | F | n-propyl | H | |
| 1.502 | H | F | n-propyl | $COCH_3$ | |
| 1.503 | H | F | $CH_2CH=CH_2$ | H | |
| 1.504 | H | F | $CH_2CH=CH_2$ | H | |
| 1.505 | H | F | n-butyl | H | |
| 1.506 | H | F | n-butyl | $COCH_3$ | |

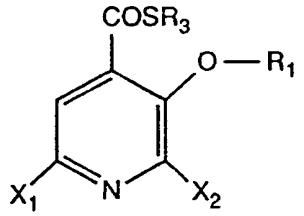
| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.507 | H | F | i-propyl | H | |
| 1.508 | H | F | i-propyl | $COCH_3$ | |
| 1.509 | H | F | i-butyl | H | |
| 1.510 | H | F | i-butyl | $COCH_3$ | |
| 1.511 | H | F | $CH_2$-$\Delta$ | H | |
| 1.512 | H | F | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.513 | H | F | $CH_2$phenyl | H | |
| 1.514 | H | F | $CH_2$phenyl | $COCH_3$ | |
| 1.515 | H | F | $CH_2$phenyl | COphenyl | |
| 1.516 | H | F | n-pentyl | H | |
| 1.517 | H | F | n-pentyl | $COCH_3$ | |
| 1.518 | H | F | cyclo$C_5H_9$ | H | |
| 1.519 | H | F | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.520 | H | F | cyc-$C_6H_{11}$ | H | |
| 1.521 | H | F | cyc-$C_6H_{11}$ | $COCH_3$ | |
| 1.522 | H | F | phenyl | H | |
| 1.523 | H | F | phenyl | $COCH_3$ | |
| 1.524 | H | F | $CH_2CF_3$ | H | |
| 1.525 | H | F | $CH_2CF_3$ | H | |
| 1.526 | H | F | $CH_2CH_2OCH_3$ | H | |
| 1.527 | H | F | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.528 | H | F | $CH_2CH_2O$phenyl | H | |
| 1.529 | H | F | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.530 | H | F | 2-F-benzyl | H | |
| 1.531 | H | F | 2-F-benzyl | $COCH_3$ | |
| 1.532 | H | F | 3-F-benzyl | H | |
| 1.533 | H | F | 3-F-benzyl | $COCH_3$ | |
| 1.534 | H | F | 4-F-benzyl | H | |
| 1.535 | H | F | 4-F-benzyl | $COCH_3$ | |
| 1.536 | H | F | 2-MeO-benzyl | H | |
| 1.537 | H | F | 2-MeO-benzyl | $COCH_3$ | |
| 1.538 | H | F | 4-MeO-benzyl | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.539 | H | F | 4-MeO-benzyl | $COCH_3$ | |
| 1.540 | H | F | $CH_2$-2-pyridyl | H | |
| 1.541 | H | F | $CH_2$-2-pyridyl | $COCH_3$ | |
| 1.542 | H | F | $CH_2$-3-pyridyl | H | |
| 1.543 | H | F | $CH_2$-3-pyridyl | $COCH_3$ | |
| 1.544 | H | F | $CH_2$-4-pyridyl | H | |
| 1.545 | H | F | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.546 | H | F | N=CH($CH_3$)phenyl | H | |
| 1.547 | H | F | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.548 | H | F | N=CH($CH_3$)-4Clphenyl | H | |
| 1.549 | H | F | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.550 | H | F | $CH_2$-2-furanyl | H | |
| 1.551 | H | F | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.552 | H | F | $CH_2$-2-thienyl | H | |
| 1.553 | H | F | $CH_2$-2-thienyl | $COCH_3$ | |
| 1.554 | H | Br | H | H | |
| 1.555 | H | Br | H | $COCH_3$ | |
| 1.556 | H | Br | H | $COCH_2CH_3$ | |
| 1.557 | H | Br | H | COPh | |
| 1.558 | H | Br | H | $CON(Et)_2$ | |
| 1.559 | H | Br | H | $CH_3$ | |
| 1.560 | H | Br | H | $CH_2Ph$ | |
| 1.561 | H | Br | $Na^+$ | H | |
| 1.562 | H | Br | $Na^+$ | $COCH_3$ | |
| 1.563 | H | Br | $NH_4^+$ | H | |
| 1.564 | H | Br | $NH_4^+$ | $COCH_3$ | |
| 1.565 | H | Br | $CH_3$ | H | |
| 1.566 | H | Br | $CH_3$ | $COCH_3$ | |
| 1.567 | H | Br | $CH_3$ | COPh | |
| 1.568 | H | Br | $CH_2CH_3$ | H | |
| 1.569 | H | Br | $CH_2CH_3$ | $COCH_3$ | |
| 1.570 | H | Br | n-propyl | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.571 | H | Br | n-propyl | $COCH_3$ | |
| 1.572 | H | Br | $CH_2CH=CH_2$ | H | |
| 1.573 | H | Br | $CH_2CH=CH_2$ | H | |
| 1.574 | H | Br | n-butyl | H | |
| 1.575 | H | Br | n-butyl | $COCH_3$ | |
| 1.576 | H | Br | i-propyl | H | |
| 1.577 | H | Br | i-propyl | $COCH_3$ | |
| 1.578 | H | Br | i-butyl | H | |
| 1.579 | H | Br | i-butyl | $COCH_3$ | |
| 1.580 | H | Br | $CH_2$-$\Delta$ | H | |
| 1.581 | H | Br | $CH_2$-$\Delta$ | $COCH_3$ | |
| 1.582 | H | Br | $CH_2$phenyl | H | |
| 1.583 | H | Br | $CH_2$phenyl | $COCH_3$ | |
| 1.584 | H | Br | $CH_2$phenyl | COphenyl | |
| 1.585 | H | Br | n-pentyl | H | |
| 1.586 | H | Br | n-pentyl | $COCH_3$ | |
| 1.587 | H | Br | cyclo$C_5H_9$ | H | |
| 1.588 | H | Br | cyc-$C_5H_9$ | $COCH_3$ | |
| 1.589 | H | Br | cyc-$C_6H_{11}$ | H | |
| 1.590 | H | Br | cyc-$C_6H_{11}$ | $COCH_3$ | |
| 1.591 | H | Br | phenyl | H | |
| 1.592 | H | Br | phenyl | $COCH_3$ | |
| 1.593 | H | Br | $CH_2CF_3$ | H | |
| 1.594 | H | Br | $CH_2CF_3$ | H | |
| 1.595 | H | Br | $CH_2CH_2OCH_3$ | H | |
| 1.596 | H | Br | $CH_2CH_2OCH_3$ | $COCH_3$ | |
| 1.597 | H | Br | $CH_2CH_2O$phenyl | H | |
| 1.598 | H | Br | $CH_2CH_2O$phenyl | $COCH_3$ | |
| 1.599 | H | Br | 2-F-benzyl | H | |
| 1.600 | H | Br | 2-F-benzyl | $COCH_3$ | |
| 1.601 | H | Br | 3-F-benzyl | H | |
| 1.602 | H | Br | 3-F-benzyl | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 1.603 | H | Br | 4-F-benzyl | H | |
| 1.604 | H | Br | 4-F-benzyl | $COCH_3$ | |
| 1.605 | H | Br | 2-MeO-benzyl | H | |
| 1.606 | H | Br | 2-MeO-benzyl | $COCH_3$ | |
| 1.607 | H | Br | 4-MeO-benzyl | H | |
| 1.608 | H | Br | 4-MeO-benzyl | $COCH_3$ | |
| 1.609 | H | Br | $CH_2$-2-pyridyl | H | |
| 1.610 | H | Br | $CH_2$-2-pyridyl | $COCH_3$ | |
| 1.611 | H | Br | $CH_2$-3-pyridyl | H | |
| 1.612 | H | Br | $CH_2$-3-pyridyl | $COCH_3$ | |
| 1.613 | H | Br | $CH_2$-4-pyridyl | H | |
| 1.614 | H | Br | $CH_2$-4-pyridyl | $COCH_3$ | |
| 1.615 | H | Br | N=CH($CH_3$)phenyl | H | |
| 1.616 | H | Br | N=CH($CH_3$)phenyl | $COCH_3$ | |
| 1.617 | H | Br | N=CH($CH_3$)-4Clphenyl | H | |
| 1.618 | H | Br | N=CH($CH_3$)4Cl-phenyl | $COCH_3$ | |
| 1.619 | H | Br | $CH_2$-2-furanyl | H | |
| 1.620 | H | Br | $CH_2$-2-furanyl | $COCH_3$ | |
| 1.621 | H | Br | $CH_2$-2-thienyl | H | |
| 1.622 | H | Br | $CH_2$-2-thienyl | $COCH_3$ | |
| 1.623 | Cl | Cl | $CH_3$ | $SO_2CH_3$ | m.p. 95-96°C |
| 1.624 | Cl | Cl | $CH_3$ | $SO_2CH_2Ph$ | oil |
| 1.625 | Cl | Cl | $CH_3$ | $SO_2N(Me)_2$ | m.p. 65-68°C |
| 1.626 | Cl | Cl | $CH_3$ | CO-4-MeO-phenyl | oil |
| 1.627 | Cl | Cl | $CH_3$ | CO-3-MeO-phenyl | oil |
| 1.628 | Cl | Cl | $CH_3$ | $CH_3$ | m.p. 74-76°C |
| 1.629 | Cl | Cl | $CH_3$ | benzyl | m.p. 77-79°C |

Table 2 : Compounds of the formula I

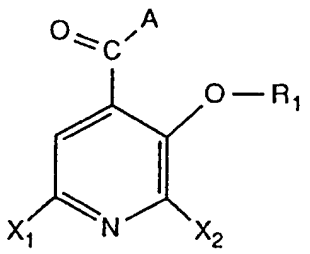



| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 2.1 | Cl | Cl | $CH_3$ | H | m.p. 115-117°C |
| 2.2 | Cl | Cl | $CH_3$ | $COCH_3$ | oil |
| 2.3 | Cl | Cl | $CH_2CH_3$ | H | |
| 2.4 | Cl | Cl | $CH_2CH_3$ | $COCH_3$ | |
| 2.5 | Cl | Cl | $CH_2CH_2CH_3$ | H | |
| 2.6 | Cl | Cl | $CH_2CH_2CH_3$ | $COCH_3$ | |
| 2.7 | Cl | Cl | benzyl | H | |
| 2.8 | Cl | Cl | benzyl | $COCH_3$ | |
| 2.9 | Br | Cl | $CH_3$ | H | |
| 2.10 | Br | Cl | $CH_3$ | $COCH_3$ | |
| 2.11 | Br | Cl | $CH_2CH_3$ | H | |
| 2.12 | Br | Cl | $CH_2CH_3$ | $COCH_3$ | |
| 2.13 | Br | Cl | $CH_2CH_2CH_3$ | H | |
| 2.14 | Br | Cl | $CH_2CH_2CH_3$ | $COCH_3$ | |
| 2.15 | Br | Cl | benzyl | H | |
| 2.16 | Br | Cl | benzyl | $COCH_3$ | |
| 2.17 | Cl | Br | $CH_3$ | H | |
| 2.18 | Cl | Br | $CH_3$ | $COCH_3$ | |
| 2.19 | Cl | Br | $CH_2CH_3$ | H | |
| 2.20 | Cl | Br | $CH_2CH_3$ | $COCH_3$ | |
| 2.21 | Cl | Br | $CH_2CH_2CH_3$ | H | |
| 2.22 | Cl | Br | $CH_2CH_2CH_3$ | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 2.23 | Cl | Br | benzyl | H | |
| 2.24 | Cl | Br | benzyl | $COCH_3$ | |
| 2.25 | Cl | F | $CH_3$ | H | |
| 2.26 | Cl | F | $CH_3$ | $COCH_3$ | |
| 2.27 | Cl | F | $CH_2CH_3$ | H | |
| 2.28 | Cl | F | $CH_2CH_3$ | $COCH_3$ | |
| 2.29 | Cl | F | $CH_2CH_2CH_3$ | H | |
| 2.30 | Cl | F | $CH_2CH_2CH_3$ | $COCH_3$ | |
| 2.31 | Cl | F | benzyl | H | |
| 2.32 | Cl | F | benzyl | $COCH_3$ | |
| 2.33 | H | Cl | $CH_3$ | H | |
| 2.34 | H | Cl | $CH_3$ | $COCH_3$ | |
| 2.35 | H | Cl | $CH_2CH_3$ | H | |
| 2.36 | H | Cl | $CH_2CH_3$ | $COCH_3$ | |
| 2.37 | H | Cl | $CH_2CH_2CH_3$ | H | |
| 2.38 | H | Cl | $CH_2CH_2CH_3$ | $COCH_3$ | |
| 2.39 | H | Cl | benzyl | H | |
| 2.40 | H | Cl | benzyl | $COCH_3$ | |
| 2.41 | Br | Br | $CH_3$ | H | |
| 2.42 | Br | Br | $CH_3$ | $COCH_3$ | |
| 2.43 | Br | Br | $CH_2CH_3$ | H | |
| 2.44 | Br | Br | $CH_2CH_3$ | $COCH_3$ | |
| 2.45 | Br | Br | $CH_2CH_2CH_3$ | H | |
| 2.46 | Br | Br | $CH_2CH_2CH_3$ | $COCH_3$ | |
| 2.47 | Br | Br | benzyl | H | |
| 2.48 | Br | Br | benzyl | $COCH_3$ | |
| 2.49 | Br | F | $CH_3$ | H | |
| 2.50 | Br | F | $CH_3$ | $COCH_3$ | |
| 2.51 | Br | F | $CH_2CH_3$ | H | |
| 2.52 | Br | F | $CH_2CH_3$ | $COCH_3$ | |
| 2.53 | Br | F | $CH_2CH_2CH_3$ | H | |
| 2.54 | Br | F | $CH_2CH_2CH_3$ | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_3$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 2.55 | Br | F | benzyl | H | |
| 2.56 | Br | F | benzyl | $COCH_3$ | |
| 2.57 | H | Br | $CH_3$ | H | |
| 2.58 | H | Br | $CH_3$ | $COCH_3$ | |
| 2.59 | H | Br | $CH_2CH_3$ | H | |
| 2.60 | H | Br | $CH_2CH_3$ | $COCH_3$ | |
| 2.61 | H | Br | $CH_2CH_2CH_3$ | H | |
| 2.62 | H | Br | $CH_2CH_2CH_3$ | $COCH_3$ | |
| 2.63 | H | Br | benzyl | H | |
| 2.64 | H | Br | benzyl | $COCH_3$ | |
| 2.65 | H | F | $CH_3$ | H | |
| 2.66 | H | F | $CH_3$ | $COCH_3$ | |
| 2.67 | H | F | $CH_2CH_3$ | H | |
| 2.68 | H | F | $CH_2CH_3$ | $COCH_3$ | |
| 2.69 | H | F | $CH_2CH_2CH_3$ | H | |
| 2.70 | H | F | $CH_2CH_2CH_3$ | $COCH_3$ | |
| 2.71 | H | F | benzyl | H | |
| 2.72 | H | F | benzyl | $COCH_3$ | |

Table 3 :



| Cmpnd. No. | $X_1$ | $X_2$ | A | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 3.1 | Cl | Cl | $NH_2$ | H | |
| 3.2 | Br | Br | $NH_2$ | H | |
| 3.3 | Br | Cl | $NH_2$ | H | |
| 3.4 | Cl | Br | $NH_2$ | H | |
| 3.5 | Cl | F | $NH_2$ | H | |
| 3.6 | Br | F | $NH_2$ | H | |
| 3.7 | H | F | $NH_2$ | H | |
| 3.8 | H | Cl | $NH_2$ | H | |
| 3.9 | H | Br | $NH_2$ | H | |
| 3.10 | Cl | Cl | $NH_2$ | $COCH_3$ | |
| 3.11 | Br | Br | $NH_2$ | $COCH_3$ | |
| 3.12 | Br | Cl | $NH_2$ | $COCH_3$ | |
| 3.13 | Cl | Br | $NH_2$ | $COCH_3$ | |
| 3.14 | Cl | F | $NH_2$ | $COCH_3$ | |
| 3.15 | Br | F | $NH_2$ | $COCH_3$ | |
| 3.16 | H | F | $NH_2$ | $COCH_3$ | |
| 3.17 | H | Cl | $NH_2$ | $COCH_3$ | |
| 3.18 | H | Br | $NH_2$ | $COCH_3$ | |
| 3.19 | Cl | Cl | $NHCH_3$ | H | |
| 3.20 | Br | Br | $NHCH_3$ | H | |
| 3.21 | Br | Cl | $NHCH_3$ | H | |
| 3.22 | Cl | Br | $NHCH_3$ | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | A | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 3.23 | Cl | F | $NHCH_3$ | H | |
| 3.24 | Br | F | $NHCH_3$ | H | |
| 3.25 | H | F | $NHCH_3$ | H | |
| 3.26 | H | Cl | $NHCH_3$ | H | |
| 3.27 | H | Br | $NHCH_3$ | H | |
| 3.28 | Cl | Cl | $NHCH_3$ | $COCH_3$ | |
| 3.29 | Br | Br | $NHCH_3$ | $COCH_3$ | |
| 3.30 | Br | Cl | $NHCH_3$ | $COCH_3$ | |
| 3.31 | Cl | Br | $NHCH_3$ | $COCH_3$ | |
| 3.32 | Cl | F | $NHCH_3$ | $COCH_3$ | |
| 3.33 | Br | F | $NHCH_3$ | $COCH_3$ | |
| 3.34 | H | F | $NHCH_3$ | $COCH_3$ | |
| 3.35 | H | Cl | $NHCH_3$ | $COCH_3$ | |
| 3.36 | H | Br | $NHCH_3$ | H | |
| 3.37 | Cl | Cl | NHEt | H | |
| 3.38 | Br | Br | NHEt | H | |
| 3.39 | Br | Cl | NHEt | H | |
| 3.40 | Cl | Br | NHEt | H | |
| 3.41 | Cl | F | NHEt | H | |
| 3.42 | Br | F | NHEt | H | |
| 3.43 | H | F | NHEt | H | |
| 3.44 | H | Cl | NHEt | H | |
| 3.45 | H | Br | NHEt | H | |
| 3.46 | Cl | Cl | NHEt | $COCH_3$ | |
| 3.47 | Br | Br | NHEt | $COCH_3$ | |
| 3.48 | Br | Cl | NHEt | $COCH_3$ | |
| 3.49 | Cl | Br | NHEt | $COCH_3$ | |
| 3.50 | Cl | F | NHEt | $COCH_3$ | |
| 3.51 | Br | F | NHEt | $COCH_3$ | |
| 3.52 | H | F | NHEt | $COCH_3$ | |
| 3.53 | H | Cl | NHEt | $COCH_3$ | |
| 3.54 | H | Br | NHEt | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | A | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 3.55 | Cl | Cl | NHOH | H | |
| 3.56 | Br | Br | NHOH | H | |
| 3.57 | Br | Cl | NHOH | H | |
| 3.58 | Cl | Br | NHOH | H | |
| 3.59 | Cl | F | NHOH | H | |
| 3.60 | Br | F | NHOH | H | |
| 3.61 | H | F | NHOH | H | |
| 3.62 | H | Cl | NHOH | H | |
| 3.63 | H | Br | NHOH | H | |
| 3.64 | Cl | Cl | NHOH | $COCH_3$ | |
| 3.65 | Br | Br | NHOH | $COCH_3$ | |
| 3.66 | Br | Cl | NHOH | $COCH_3$ | |
| 3.67 | Cl | Br | NHOH | $COCH_3$ | |
| 3.68 | Cl | F | NHOH | $COCH_3$ | |
| 3.69 | Br | F | NHOH | $COCH_3$ | |
| 3.70 | H | F | NHOH | $COCH_3$ | |
| 3.71 | H | Cl | NHOH | $COCH_3$ | |
| 3.72 | H | Br | NHOH | $COCH_3$ | |
| 3.73 | Cl | Cl | $NHOCH_3$ | H | |
| 3.74 | Br | Br | $NHOCH_3$ | H | |
| 3.75 | Br | Cl | $NHOCH_3$ | H | |
| 3.76 | Cl | Br | $NHOCH_3$ | H | |
| 3.77 | Cl | F | $NHOCH_3$ | H | |
| 3.78 | Br | F | $NHOCH_3$ | H | |
| 3.79 | H | F | $NHOCH_3$ | H | |
| 3.80 | H | Cl | $NHOCH_3$ | H | |
| 3.81 | H | Br | $NHOCH_3$ | H | |
| 3.82 | Cl | Cl | $NHOCH_3$ | $COCH_3$ | |
| 3.83 | Br | Br | $NHOCH_3$ | $COCH_3$ | |
| 3.84 | Br | Cl | $NHOCH_3$ | $COCH_3$ | |
| 3.85 | Cl | Br | $NHOCH_3$ | $COCH_3$ | |
| 3.86 | Cl | F | $NHOCH_3$ | $COCH_3$ | |

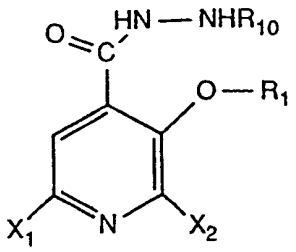
| Cmpnd. No. | $X_1$ | $X_2$ | A | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 3.87 | Br | F | $NHOCH_3$ | $COCH_3$ | |
| 3.88 | H | F | $NHOCH_3$ | $COCH_3$ | |
| 3.89 | H | Cl | $NHOCH_3$ | $COCH_3$ | |
| 3.90 | H | Br | $NHOCH_3$ | $COCH_3$ | |
| 3.91 | Cl | Cl | NHbenzyl | H | |
| 3.92 | Br | Br | NHbenzyl | H | |
| 3.93 | Br | Cl | NHbenzyl | H | |
| 3.94 | Cl | Br | NHbenzyl | H | |
| 3.95 | Cl | F | NHbenzyl | H | |
| 3.96 | Br | F | NHbenzyl | H | |
| 3.97 | H | F | NHbenzyl | H | |
| 3.98 | H | Cl | NHbenzyl | H | |
| 3.99 | H | Br | NHbenzyl | H | |
| 3.100 | Cl | Cl | NHbenzyl | $COCH_3$ | |
| 3.101 | Br | Br | NHbenzyl | $COCH_3$ | |
| 3.102 | Br | Cl | NHbenzyl | $COCH_3$ | |
| 3.103 | Cl | Br | NHbenzyl | $COCH_3$ | |
| 3.104 | Cl | F | NHbenzyl | $COCH_3$ | |
| 3.105 | Br | F | NHbenzyl | $COCH_3$ | |
| 3.106 | H | F | NHbenzyl | $COCH_3$ | |
| 3.107 | H | Cl | NHbenzyl | $COCH_3$ | |
| 3.108 | H | Br | NHbenzyl | $COCH_3$ | |
| 3.109 | Cl | Cl | $NHCH(CH_3)COOCH_3$ | H | m.p. 130-131°C (S isomer) |
| 3.110 | Br | Br | $NHCH(CH_3)COOCH_3$ | H | |
| 3.111 | Br | Cl | $NHCH(CH_3)COOCH_3$ | H | |
| 3.112 | Cl | Br | $NHCH(CH_3)COOCH_3$ | H | |
| 3.113 | Cl | F | $NHCH(CH_3)COOCH_3$ | H | |
| 3.114 | Br | F | $NHCH(CH_3)COOCH_3$ | H | |
| 3.115 | H | F | $NHCH(CH_3)COOCH_3$ | H | |
| 3.116 | H | Cl | $NHCH(CH_3)COOCH_3$ | H | |
| 3.117 | H | Br | $NHCH(CH_3)COOCH_3$ | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | A | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 3.118 | Cl | Cl | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.119 | Br | Br | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.120 | Br | Cl | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.121 | Cl | Br | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.122 | Cl | F | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.123 | Br | F | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.124 | H | F | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.125 | H | Cl | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.126 | H | Br | $NHCH(CH_3)COOCH_3$ | $COCH_3$ | |
| 3.127 | Cl | Cl | $NHCH(CH_3)COO$benzyl | H | |
| 3.128 | Br | Br | $NHCH(CH_3)COO$benzyl | H | |
| 3.129 | Br | Cl | $NHCH(CH_3)COO$benzyl | H | |
| 3.130 | Cl | Br | $NHCH(CH_3)COO$benzyl | H | |
| 3.131 | Cl | F | $NHCH(CH_3)COO$benzyl | H | |
| 3.132 | Br | F | $NHCH(CH_3)COO$benzyl | H | |
| 3.133 | H | F | $NHCH(CH_3)COO$benzyl | H | |
| 3.134 | H | Cl | $NHCH(CH_3)COO$benzyl | H | |
| 3.135 | H | Br | $NHCH(CH_3)COO$benzyl | H | |
| 3.136 | Cl | Cl | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.137 | Br | Br | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.138 | Br | Cl | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.139 | Cl | Br | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.140 | Cl | F | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.141 | Br | F | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.142 | H | F | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.143 | H | Cl | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.144 | H | Br | $NHCH(CH_3)COO$benzyl | $COCH_3$ | |
| 3.145 | Cl | Cl | $NHCH(i\text{-prop.})COOCH_3$ | H | m.p. 87-89°C (S isomer) |
| 3.146 | Br | Br | $NHCH(i\text{-prop.})COOCH_3$ | H | |
| 3.147 | Br | Cl | $NHCH(i\text{-prop.})COOCH_3$ | H | |
| 3.148 | Cl | Br | $NHCH(i\text{-prop.})COOCH_3$ | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | A | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 3.149 | Cl | F | NHCH(i-prop.)$COOCH_3$ | H | |
| 3.150 | Br | F | NHCH(i-prop.)$COOCH_3$ | H | |
| 3.151 | H | F | NHCH(i-prop.)$COOCH_3$ | H | |
| 3.152 | H | Cl | NHCH(i-prop.)$COOCH_3$ | H | |
| 3.153 | H | Br | NHCH(i-prop.)$COOCH_3$ | H | |
| 3.154 | Cl | Cl | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.155 | Br | Br | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.156 | Br | Cl | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.157 | Cl | Br | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.158 | Cl | F | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.159 | Br | F | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.160 | H | F | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.161 | H | Cl | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.162 | H | Br | NHCH(i-prop.)$COOCH_3$ | $COCH_3$ | |
| 3.163 | Cl | Cl | NHCH(i-Pr)COObenzyl | H | |
| 3.164 | Br | Br | NHCH(i-Pr)COObenzyl | H | |
| 3.165 | Br | Cl | NHCH(i-Pr)COObenzyl | H | |
| 3.166 | Cl | Br | NHCH(i-Pr)COObenzyl | H | |
| 3.167 | Cl | F | NHCH(i-Pr)COObenzyl | H | |
| 3.168 | Br | F | NHCH(i-Pr)COObenzyl | H | |
| 3.169 | H | F | NHCH(i-Pr)COObenzyl | H | |
| 3.170 | H | Cl | NHCH(i-Pr)COObenzyl | H | |
| 3.171 | H | Br | NHCH(i-Pr)COObenzyl | H | |
| 3.172 | Cl | Cl | NHCH(i-Pr)COObenzyl | $COCH_3$ | |
| 3.173 | Br | Br | NHCH(i-Pr)COObenzyl | $COCH_3$ | |
| 3.174 | Br | Cl | NHCH(i-Pr)COObenzyl | $COCH_3$ | |
| 3.175 | Cl | Br | NHCH(i-Pr)COObenzyl | $COCH_3$ | |
| 3.176 | Cl | F | NHCH(i-Pr)COObenzyl | $COCH_3$ | |
| 3.177 | Br | F | NHCH(i-Pr)COObenzyl | $COCH_3$ | |
| 3.178 | H | F | NHCH(i-Pr)COObenzyl | $COCH_3$ | |
| 3.179 | H | Cl | NHCH(i-Pr)COObenzyl | $COCH_3$ | |
| 3.180 | H | Br | NHCH(i-Pr)COObenzyl | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | A | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 3.181 | Cl | Cl | $N(Et)_2$ | $CON(Et)_2$ | m.p. 83-85°C |
| 3.182 | Br | Br | $N(Et)_2$ | $CON(Et)_2$ | m.p.106-108°C |
| 3.183 | Br | Cl | $N(Et)_2$ | $CON(Et)_2$ | |
| 3.184 | Cl | Br | $N(Et)_2$ | $CON(Et)_2$ | |
| 3.185 | Cl | F | $N(Et)_2$ | $CON(Et)_2$ | |
| 3.186 | Br | F | $N(Et)_2$ | $CON(Et)_2$ | |
| 3.187 | H | F | $N(Et)_2$ | $CON(Et)_2$ | oil |
| 3.188 | H | Cl | $N(Et)_2$ | $CON(Et)_2$ | oil |
| 3.189 | H | Br | $N(Et)_2$ | $CON(Et)_2$ | |
| 3.190 | Cl | Cl | $N(Et)_2$ | H | m.p. 122-124°C |
| 3.191 | Cl | Cl | $N(Et)_2$ | $CSN(Et)_2$ | m.p. 65-68°C |
| 3.192 | H | F | $N(Et)_2$ | H | m.p.180-183°C |

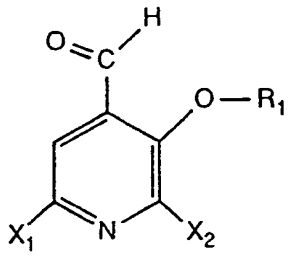
Table 4 :




| Cmpnd. No. | $X_1$ | $X_2$ | $R_{10}$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 4.1 | Cl | Cl | phenyl | H | |
| 4.2 | Br | Br | phenyl | H | |
| 4.3 | Br | Cl | phenyl | H | |
| 4.4 | Cl | Br | phenyl | H | |
| 4.5 | Cl | F | phenyl | H | |
| 4.6 | Br | F | phenyl | H | |
| 4.7 | H | F | phenyl | H | |
| 4.8 | H | Cl | phenyl | H | |
| 4.9 | H | Br | phenyl | H | |
| 4.10 | Cl | Cl | phenyl | $COCH_3$ | |
| 4.11 | Br | Br | phenyl | $COCH_3$ | |
| 4.12 | Br | Cl | phenyl | $COCH_3$ | |
| 4.13 | Cl | Br | phenyl | $COCH_3$ | |
| 4.14 | Cl | F | phenyl | $COCH_3$ | |
| 4.15 | Br | F | phenyl | $COCH_3$ | |
| 4.16 | H | F | phenyl | $COCH_3$ | |
| 4.17 | H | Cl | phenyl | $COCH_3$ | |
| 4.18 | H | Br | phenyl | $COCH_3$ | |
| 4.19 | Cl | Cl | 2,4,6-tri-Cl-phenyl | H | |
| 4.20 | Br | Br | 2,4,6-tri-Cl-phenyl | H | |
| 4.21 | Br | Cl | 2,4,6-tri-Cl-phenyl | H | |
| 4.22 | Cl | Br | 2,4,6-tri-Cl-phenyl | H | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_{10}$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 4.23 | Cl | F | 2,4,6-tri-Cl-phenyl | H | |
| 4.24 | Br | F | 2,4,6-tri-Cl-phenyl | H | |
| 4.25 | H | F | 2,4,6-tri-Cl-phenyl | H | |
| 4.26 | H | Cl | 2,4,6-tri-Cl-phenyl | H | |
| 4.27 | H | Br | 2,4,6-tri-Cl-phenyl | H | |
| 4.28 | Cl | Cl | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |
| 4.29 | Br | Br | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |
| 4.30 | Br | Cl | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |
| 4.31 | Cl | Br | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |
| 4.32 | Cl | F | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |
| 4.33 | Br | F | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |
| 4.34 | H | F | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |
| 4.35 | H | Cl | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |
| 4.36 | H | Br | 2,4,6-tri-Cl-phenyl | $COCH_3$ | |

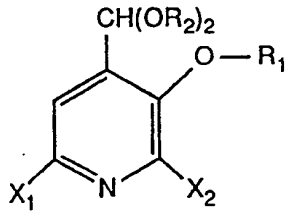
Table 5 :



| Cmpnd. No. | $X_1$ | $X_2$ | $R_1$ | Phys. data |
|---|---|---|---|---|
| 5.1 | Cl | Cl | H | m.p. 104-106°C |
| 5.2 | Br | Br | H | |
| 5.3 | Br | Cl | H | |
| 5.4 | Cl | Br | H | |
| 5.5 | Cl | F | H | |
| 5.6 | Br | F | H | |
| 5.7 | H | F | H | |
| 5.8 | H | Cl | H | |
| 5.9 | H | Br | H | |
| 5.10 | Cl | Cl | $COCH_3$ | m.p. 61-62°C |
| 5.11 | Br | Br | $COCH_3$ | |
| 5.12 | Br | Cl | $COCH_3$ | |
| 5.13 | Cl | Br | $COCH_3$ | |
| 5.14 | Cl | F | $COCH_3$ | |
| 5.15 | Br | F | $COCH_3$ | |
| 5.16 | H | F | $COCH_3$ | |
| 5.17 | H | Cl | $COCH_3$ | |
| 5.18 | H | Br | $COCH_3$ | |
| 5.19 | Cl | Cl | $CONEt_2$ | oil |
| 5.20 | Br | Br | $CONEt_2$ | |
| 5.21 | Br | Cl | $CONEt_2$ | |
| 5.22 | Cl | Br | $CONEt_2$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_1$ | Phys. data |
|---|---|---|---|---|
| 5.23 | Cl | F | $CONEt_2$ | |
| 5.24 | Br | F | $CONEt_2$ | |
| 5.25 | H | F | $CONEt_2$ | |
| 5.26 | H | Cl | $CONEt_2$ | |
| 5.27 | H | Br | $CONEt_2$ | |

Table 6 :




| Cmpnd. No. | $X_1$ | $X_2$ | $R_2$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 6.1 | Cl | Cl | $-CH_2CH_2-$ | H | m.p. 92-94°C |
| 6.2 | Br | Br | $-CH_2CH(CH_2OH)-$ | H | |
| 6.3 | Br | Cl | $-CH_2CH_2-$ | H | |
| 6.4 | Cl | Br | $-CH_2CH_2-$ | H | |
| 6.5 | Cl | F | $-CH_2CH_2-$ | H | |
| 6.6 | Br | F | $-CH_2CH_2-$ | H | |
| 6.7 | H | F | $-CH_2CH_2-$ | H | |
| 6.8 | H | Cl | $-CH_2CH_2-$ | H | |
| 6.9 | H | Br | $-CH_2CH(CH_3)-$ | H | |
| 6.10 | Cl | Cl | $-CH_2CH_2-$ | $COCH_3$ | m.p. 50-52°C |
| 6.11 | Br | Br | $-CH_2CH_2-$ | $COCH_3$ | |
| 6.12 | Br | Cl | $-CH_2CH_2-$ | $COCH_3$ | |
| 6.13 | Cl | Br | $-CH_2CH_2-$ | $COCH_3$ | |
| 6.14 | Cl | F | $-CH_2CH_2-$ | $COCH_3$ | |
| 6.15 | Br | F | $-CH_2CH_2-$ | $COCH_3$ | |
| 6.16 | H | F | $-CH_2CH_2-$ | $COCH_3$ | |
| 6.17 | H | Cl | $-CH_2CH_2-$ | $COCH_3$ | |
| 6.18 | H | Br | $-CH_2CH_2-$ | $COCH_3$ | |
| 6.19 | Cl | Cl | $-CH_2CH_2-$ | $CONEt_2$ | oil |
| 6.20 | Br | Br | $-CH_2CH_2-$ | $CONEt_2$ | |
| 6.21 | Br | Cl | $-CH_2CH_2-$ | $CONEt_2$ | |
| 6.22 | Cl | Br | $-CH_2CH_2-$ | $CONEt_2$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_2$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 6.23 | Cl | F | $-CH_2CH_2-$ | $CONEt_2$ | |
| 6.24 | Br | F | $-CH_2CH_2-$ | $CONEt_2$ | |
| 6.25 | H | F | $-CH_2CH_2-$ | $CONEt_2$ | |
| 6.26 | H | Cl | $-CH_2CH_2-$ | $CONEt_2$ | |
| 6.27 | H | Br | $-CH_2CH_2-$ | $CONEt_2$ | |
| 6.28 | Cl | Cl | $-CH_2CH_3$ | H | |
| 6.29 | Br | Br | $-CH_2CH_3$ | H | |
| 6.30 | Br | Cl | $-CH_2CH_3$ | H | |
| 6.31 | Cl | Br | $-CH_2CH_3$ | H | |
| 6.32 | Cl | F | $-CH_2CH_3$ | H | |
| 6.33 | Br | F | $-CH_2CH_3$ | H | |
| 6.34 | H | F | $-CH_2CH_3$ | H | |
| 6.35 | H | Cl | $-CH_2CH_3$ | H | |
| 6.36 | H | Br | $-CH_2CH_3$ | H | |
| 6.37 | Cl | Cl | $-CH_2CH_3$ | $COCH_3$ | |
| 6.38 | Br | Br | $-CH_2CH_3$ | $COCH_3$ | |
| 6.39 | Br | Cl | $-CH_2CH_3$ | $COCH_3$ | |
| 6.40 | Cl | Br | $-CH_2CH_3$ | $COCH_3$ | |
| 6.41 | Cl | F | $-CH_2CH_3$ | $COCH_3$ | |
| 6.42 | Br | F | $-CH_2CH_3$ | $COCH_3$ | |
| 6.43 | H | F | $-CH_2CH_3$ | $COCH_3$ | |
| 6.44 | H | Cl | $-CH_2CH_3$ | $COCH_3$ | |
| 6.45 | H | Br | $-CH_2CH_3$ | $COCH_3$ | |
| 6.46 | Cl | Cl | $COCH_3$ | $COCH_3$ | m.p. 90-92°C |
| 6.47 | Br | Br | $COCH_3$ | $COCH_3$ | |
| 6.48 | Br | Cl | $COCH_3$ | $COCH_3$ | |
| 6.49 | Cl | Br | $COCH_3$ | $COCH_3$ | |
| 6.50 | Cl | F | $COCH_3$ | $COCH_3$ | |
| 6.51 | Br | F | $COCH_3$ | $COCH_3$ | |
| 6.52 | H | F | $COCH_3$ | $COCH_3$ | |
| 6.53 | H | Cl | $COCH_3$ | $COCH_3$ | |
| 6.54 | H | Br | $COCH_3$ | $COCH_3$ | |

| Cmpnd. No. | $X_1$ | $X_2$ | $R_2$ | $R_1$ | Phys. data |
|---|---|---|---|---|---|
| 6.55 | Cl | Cl | $-CH_2CH(CH_2OH)-$ | H | |
| 6.56 | Cl | Cl | $-CH_3$ | H | m.p. 65-67°C |
| 6.57 | Cl | Cl | $-CH_2CH_3$ | H | |
| 6.58 | Cl | Cl | $-CH_3$ | $COCH_3$ | m.p. 58-60°C |
| 6.59 | Cl | Cl | $-CH_2CH_3$ | $COCH_3$ | |

2. Formulation examples for liquid active compounds of formula I (% = per cent by weight)

| 2.1 Emulsion concentrates | a) | b) | c) |
|---|---|---|---|
| Active compound from Tables 1 to 6 | 25 % | 40 % | 50 % |
| Calcium dodecylbenzenesulfonate | 5 % | 8 % | 6 % |
| Castor oil polyethylene glycol ether (36 mol of ethylene oxide) | 5 % | - | - |
| Tributylphenoyl polyethylene glycol ether (30 mol of ethylene oxide | - | 12 % | 4 % |
| Cyclohexanone | - | 15 % | 20 % |
| Xylene mixture | 65 % | 25 % | 20 % |

Emulsions of any desired concentration may be prepared from these concentrates by diluting with water.

| 2.2 Solutions | a) | b) | c) | d) |
|---|---|---|---|---|
| Active compound from Tables 1 to 6 | 80 % | 10 % | 5 % | 95 % |
| Ethylene glycol monomethyl ether | 20 % | - | - | - |
| Polyethylene glycol MW 400 | - | 70 % | - | - |
| N-Methyl-2-pyrrolidone | - | 20 % | - | - |
| Epoxidated coconut oil | - | - | 1 % | 5 % |
| Petrol (boiling limits 160-190°C) | - | - | 94 % | - |

(MW = molecular weight)

The solutions are suitable for use in the form of very small drops.

| 2.3 Granules | a) | b) |
|---|---|---|
| Active compound from Tables 1 to 6 | 5 % | 10 % |
| Kaolin | 94 % | - |
| Highly disperse silicic acid | 1 % | - |
| Attapulgite | - | 90 % |

The active compound is dissolved in methylene chloride and this solution is sprayed onto the support and the solvent is subsequently evaporated off in vacuo.

| 2.4 Dusting compositions | a) | b) |
|---|---|---|
| Active compound from Tables 1 to 6 | 2 % | 5 % |
| Highly disperse silicic acid | 1 % | 5 % |
| Talc | 97 % | - |
| Kaolin | - | 90 % |

Ready-to-use dusting compositions are obtained by intimately mixing the excipients with the active compound.

Formulation examples for solid active compounds of the formula I (% = per cent by weight)

| 2.5 Wettable powders | a) | b) | c) |
|---|---|---|---|
| Active compound from Tables 1 to 6 | 25 % | 50 % | 75 % |
| Sodium lignosulfonate | 5 % | 5 % | |
| Sodium lauryl sulfate | 3 % | - | 5 % |
| Sodium diisobutylnaphthalene-sulfonate | - | 6 % | 10 % |
| Octylphenol polyethylene glycol ether (7-8 mol of ethylene oxide) | - | 2 % | - |
| Highly disperse silicic acid | 5 % | 10 % | 10 % |
| Kaolin | 62 % | 27 % | - |

The active compound is mixed with the additives and ground homogeneously in a suitable mill. Wettable powders are obtained which can be diluted with water to give suspensions of any desired concentration.

| 2.6 Emulsion concentrate | |
|---|---|
| Active compound from Tables 1 to 6 | 10 % |
| Octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide) | 3 % |
| Calcium dodecylbenzenesulfonate | 3 % |
| Castor oil polyglycol ether (35 mol of ethylene oxide | 4 % |
| Cyclohexanone | 30 % |
| Xylene mixture | 50 % |

Emulsions of any desired concentration may be prepared from this concentrate by diluting with water.

| 2.7 Dusting compositions | a) | b) |
|---|---|---|
| Active compound from Tables 1 to 6 | 5 % | 8 % |
| Talc | 95 % | - |
| Kaolin | - | 92 % |

Ready-to-use dusting compositions are obtained by mixing the active compound with the excipients and grinding on a suitable mill.

| 2.8 Extruder granules | |
|---|---|
| Active compound from Tables 1 to 6 | 10 % |
| Sodium lignosulfonate | 2 % |
| Carboxymethylcellulose | 1 % |
| Kaolin | 87 % |

The active compound is mixed with the additives, ground and moistened with water. This mixture is extruded and then dried in a current of air.

| 2.9 Coating granules | |
|---|---|
| Active compound from Tables 1 to 6 | 3 % |
| Polyethylene glycol (MW 200) | 3 % |
| Kaolin | 94 % |
| (MW = molecular weight) | |

The finely ground active compound is applied uniformly, in a mixer, to the kaolin which has been moistened with polyethylene glycol. Dust-free coating granules are obtained in this manner.

| 2.10 Suspension concentrate | |
|---|---|
| Active compound from Tables 1 to 6 | 40 % |
| Ethylene glycol | 10 % |
| Nonylphenol polyethylene glycol ether | 6 % |
| (15 mol of ethylene oxide) | |

| | |
|---|---|
| Sodium lignosulfonate | 10 % |
| Carboxymethylcellulose | 1 % |
| 37 % aqueous solution of formaldehyde | 0.2 % |
| Silicone oil in the form of a 75 % aqueous emulsion | 0.8 % |
| Water | 32 % |

The finely ground active compound is mixed intimately with the additives. A suspension concentrate is obtained from which suspensions of any desired concentration may be prepared by diluting with water.

3. Biological examples

Example 3.1: Effect against Colletotrichum lagenarium on Cucumis sativus L.

a) Residual protective effect

After having been cultivated for 10 days, cucumber plants are sprayed with a spray liquor (concentration: 200 ppm) which has been prepared from a wettable powder of the active compound.

After 24-96 hours, the plants are infected with a spore suspension (approximately $1.5 \times 10^5$ spores/ml) of the fungus and incubated at a temperature of 23°C for 30 hours at high atmospheric humidity. The incubation is then continued at normal atmospheric humidity and at from 22°C to 23°C.

10 days after the infection, the protective effect is assessed on the basis of the fungal infestation.

b) Systemic effect

After having been cultivated for 10 days, cucumber plants are treated, by means of application to the soil, with a spray liquor which has been prepared from a wettable powder of the active compound (concentration: 60 or 20 ppm based on the soil volume).

After 48-72 hours, the plants are infected with a spore suspension (approximately $1.5 \times 10^5$ spores/ml) of the fungus and incubated at a temperature of 23°C for 30 hours at high atmospheric humidity. The incubation is then continued at normal atmospheric humidity and at 22°C.

10 days after the infection, the protective effect is assessed on the basis of the fungal infestation.

In tests (a) and (b), compounds from Tables 1 to 6 exhibited a protective effect against infestation with Colletotrichum. Thus, compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46, for example, brought about a substantial reduction in fungal infestation. By contrast, untreated but infected control plants exhibited 100 % infestation with Colletotrichum.

Example 3.2: Effect against Puccinia graminis on wheat

a) Residual protective effect

6 days after having been planted, wheat plants are sprayed with a spray liquor (0.02 % active substance) which has been prepared from a wettable powder of the active compound. After 24 hours, the treated plants are infected with an uredo spore suspension of the fungus. After a 48-hour incubation at 95-100 % relative atmospheric humidity and at approximately 20°C, the infected plants are placed in a greenhouse at approximately 22°C. The development of rust pustules is assessed at 12 days after the infection.

b) Systemic effect

A spray liquor (0.006 % active substance based on the soil volume) which has been prepared from a wettable powder of the active compound is supplied by pouring to wheat plants 5 days after they have been planted. After 48-72 hours, the treated plants are infected with an urediospore suspension of the fungus. After a 48-hour incubation at 95-100 % relative atmospheric humidity and at approximately 20°C, the infected plants are placed in a greenhouse at approximately 22°C. The development of rust pustules is assessed at 12 days after the infection.

Example 3.3: Effect against Phytophthora infestans on tomato plants

a) Residual protective effect

After having been cultivated for 3 weeks, tomato plants are sprayed with a spray liquor (0.02 % active substance) which has been prepared from a wettable powder of the active compound. After 24 hours, the treated plants are infected with a spore suspension of the fungus. The fungal infestation was assessed after incubating the infected plants for 24-96 hours at 90-100 % relative atmospheric humidity and at 20°C.

b) Systemic effect

A spray liquor (0.002 % active substance based on the soil volume) which has been prepared from a wettable powder of the active compound is supplied by pouring to tomato plants after they have been cultivated for 3 weeks. Care is taken, in this context, to ensure that the spray liquor does not come into contact with the parts of the plants which are above the soil. After 48-72 hours, the treated plants are infected with a spore suspension of the fungus. The fungal infestation is assessed after incubating the infected plants for 24-96 hours at 90-100 % relative atmospheric humidity and at 20°C.

Compounds from Tables 1 to 6 exhibited a good systemic effect against the Phytophthora fungus. Thus, in test (a), for example, the compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46 reduced the fungal infestation down to 0 to 20 %. By contrast, untreated but infected control plants exhibited a 100 % infestation with Phytophthora.

Example 3.4: Effect against Plasmopara viticola on grapevines

Residual protective effect

Grapevine seedlings are sprayed, at the 4-5 leaf stage, with a spray liquor (0.02 % active substance) which has been prepared from a wettable powder of the active compound. After 24 hours, the treated plants are infected with a sporangial suspension of the fungus. The fungal infestation is assessed after incubating for 6 days at 95-100 % relative atmospheric humidity and at 20°C.

Compounds from Tables 1 to 6 substantially prevented infestation with Plasmopara viticola. By contrast, untreated but infected control plants exhibited a 100 % infestation with Plasmopara.

Example 3.5: Effect against Piricularia oryzae on rice plants

a) Residual protective effect

After having been cultivated for 2 weeks, rice plants are sprayed with a spray liquor (0.02 % active substance) which has been prepared from a wettable powder of the active compound. After 48 hours, the treated plants are infected with a conidial suspension of the fungus. The fungal infestation is assessed after incubating for 5 days at 95-100 % relative atmospheric humidity and at 24°C.

b) Systemic effect: A spray liquor (0.006% active substance based on the soil volume)

which has been prepared from a wettable powder of the active compound is supplied by pouring to 18 day-old rice plants. After that, the pots are filled with water to such an extent that the lowest parts of the rice plant stems are standing in the water. After 96-120 hours, the treated rice plants are infected with a conidial suspension of the fungus. The fungal infestation is assessed after the infected plants have been incubated for 5 days at 100 % relative atmospheric humidity and at approximately 24°C.

In comparison with untreated control plants (100 % infestation), rice plants which were treated with a spray liquor which contained a compound from Tables 1 to 6 as the active substance exhibited only a low fungal infestation. Thus, in test (a), for example, the compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46 reduced the fungal infestation down to 5 to 20 %.

Example 3.6: Effect against Pseudomonas lachrymans on Cucumis sativus L.

a) Residual protective effect

After having been cultivated for 10 days, cucumber plants are sprayed with a spray liquor (concentration: 200 ppm) which has been prepared from a wettable powder of the active compound.

After 72 hours, the plants are infected with a bacterial suspension (approximately $10^8$ spores/ml) and incubated for 7 days at high atmospheric humidity and at a temperature of 23°C.

10 days after the infection, the protective effect is assessed on the basis of the fungal infestation.

b) Systemic effect

After having been cultivated for 10 days, cucumber plants are treated, by means of application to the soil, with a spray liquor which has been prepared from a wettable powder of the active compound (concentration: 60 or 20 ppm based on the soil volume).

After 72 hours, the plants are infected with a bacterial suspension (approximately $10^8$ spores/ml) and incubated for 7 days at high atmospheric humidity and at a temperature of 23°C.

10 days after the infection, the protective effect is assessed on the basis of the bacterial infestation.

In tests (a) and (b), compounds from Tables 1 to 6 exhibited a good protective effect against infestation with Pseudomonas. Thus, the compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46, for example, reduced bacterial infestation down to 0 to 10 %. By contrast, untreated but infected control plants exhibited a 100 % infestation with Pseudomonas.

Example 3.7: Immunizing effect against tobacco mosaic virus on tobacco

8 week-old tobacco plants are sprayed (concentration: 200 ppm) or injected (concentration: 200 ppm) with a formulated solution of the active compound. After 4 days, the plants are inoculated mechanically with a suspension of tobacco mosaic virus (0.5 µg/ml + carborundum) and incubated at a temperature of 20°-22°C.

7 days after the inoculation, the protective effect is assessed on the basis of the number and size of the local lesions.

Compounds from Tables 1 to 6 evoked good immunization against tobacco mosaic virus, with compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46, for example, to a large extent preventing viral infestation. By contrast, infected but untreated control plants exhibited 100 % lesions.

Example 3.8: Effect against Xanthomonas oryzae on rice (Oryza sativa)

a) Residual protective effect

After having been cultivated for 3 weeks in a greenhouse, rice plants are sprayed with the test substance in the form of a spray liquor (0.02 % active substance). After this spray coating has dried on for one day, the plants are placed in a climate chamber at 24°C and 75-85 % relative atmospheric humidity, and infected. The infection is achieved by cutting off the leaf tips with a pair of scissors which has previously been immersed in a suspension of Xanthomonas oryzae. After having been incubated for 10 days, the cut leaves, if infested, wilt, roll up and become necrotic. The extent of these disease symptoms is used to assess the residual activity of the test substance.

b) Systemic effect

After having been cultivated in a greenhouse for 3 weeks, a suspension of the test substance is supplied to rice plants by pouring such that the rice plant itself is not wetted (0.006 % active substance based on the soil volume). Three days after this treatment, the plants are placed in a climate chamber at 24°C and 75-85 % relative atmospheric humidity, and infected. The infection is achieved by cutting off the leaf tips with a pair of scissors which has previously been immersed in a suspension of Xanthomonas oryzae. After having been incubated for 10 days, the cut leaves, if infested, wilt, roll up and become necrotic. The extent of these disease symptoms is used to assess the systemic activity of the test substance.

Compounds from Tables 1 to 6 exhibited a good effect against Xanthomonas oryzae. Thus, in tests (a) and (b), for example, compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46 reduced fungal infestation down to 0 to 20 %. By contrast, untreated but infected control plants exhibited a 100 % attack by the disease.

Example 3.9: Effect against Xanthomonas vesicatoria on pepper (Capsicum annuum)

a) Residual protective effect

After having been cultivated for 3 weeks in a greenhouse, pepper plants of the "California Wonder" variety are sprayed with the test substance in the form of a spray liquor (0.02 % active substance). After this spray coating has dried on for one day, the plants are placed in a climate chamber at 26°C and 95-100 % relative atmospheric humidity and infected by spraying the undersides of the leaves with a standardized suspension of Xanthomonas vesicatoria. After 6 days of incubation, round, initially watery, subsequently necrotic, bright spots are formed on the leaves, if they are infested. The extent of these spots is used to assess the residual activity of the test substance.

b) Systemic effect

After having been cultivated for 3 weeks in a greenhouse, pepper plants of the "California Wonder" variety are watered with a suspension of the test substance (0.006 % active substance based on the soil volume). Three days after this treatment, the plants are placed in a climate chamber at 26°C and 95-100 % relative atmospheric humidity and infected by spraying the undersides of the leaves with a standardized suspension of Xanthomonas vesicatoria. After incubating for 6 days, round, initially watery, subsequently necrotic, bright spots are formed on the leaves, if they are infested. The extent of these spots is used

to assess the systemic activity of the test substance.

Compounds from Tables 1 to 6 exhibited clear prevention of infestation by Xanthomonas vesicatoria. Thus, compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46, for example, reduced infestation with bacteria down to 0 to 20 % in tests a) and b). By contrast, untreated but infected control plants exhibited 100 % attack by the disease.

Example 3.10: Dressing effect against Fusarium nivale on rye

Rye of the Tetrahell variety, which has been naturally infected with Fusarium nivale, is dressed with the test substance on a mixing roller, with the following concentrations being used: 600, 200 or 60 ppm of active substance (based on the weight of the seed).

In October, the infected and treated rye is sown, using a sowing machine, in the open ground on plots of 3 m in length and having 6 rows of seeds, with there being 3 repetitions per experimental product.

Until infestation is assessed, the experimental plantation is cultivated under normal field conditions (preferably in a region where there is a complete covering of snow during the winter months).

In order to ascertain the activity of the active compound, the percentage proportion of plants which are infested with Fusarium is determined in the spring immediately after the snow has melted.

Compounds from Tables 1 to 6 exhibited an effect against Fusarium. Untreated but infected control plants exhibited a 100 % attack by the disease.

Example 3.11: Dressing effect against Helminthosporium gramineum on barley

Winter barley of the "C1" variety, which has been naturally infected with Helminthosporium gramineum, is dressed with the test substance on a mixing roller, with the following concentrations being used: 600, 200 or 60 ppm of active substance (based on the weight of the seed).

In October, the infected and treated barley is sown, using a sowing machine, in the open ground on plots of 2 m in length and having 3 rows of seeds, with there being 3 repetitions

per experimental plot.

Until infestation is assessed, the experimental plantation is cultivated under normal field conditions.

In order to ascertain the activity of the active compound, the percentage proportion of stems which are infested with Helminthospora is determined at the time of earing up.

Compounds from Tables 1 to 6 to a large extent prevented infestation with Helminthosporium. Untreated but infected control plants exhibited a 100 % attack by the disease.

Example 3.12: Dressing effect against Ustilago nuda on barley

Winter barley of the "RM1" variety, which has been naturally infected with Ustilago nuda, is dressed with the test substance on a mixing roller, with the following concentrations being used: 600, 200 or 60 ppm of active substance (based on the weight of the seed).

In October, the infected and treated barley is sown, using a sowing machine, in the open ground on plots of 2 m in length and having 3 rows of seeds, with there being 3 repetitions per experimental product.

Until infestation is assessed, the experimental plantation is cultivated under normal field conditions.

In order to ascertain the activity of the active compound, the percentage proportion of ears which are infested with Ustilago is determined during flowering.

Compounds from Tables 1 to 6 exhibited an effect against Ustilago. Untreated but infected control plants exhibited a 100 % attack by the disease.

Example 3.13: Dressing effect against Colletotrichum lagenarium on Cucumis sativus L.

Cucumber seeds are dressed with a solution of the active compound (concentration: 180 g/100 kg of seed). These seeds are sown. After 4 weeks, the plants are infected with a spore suspension (approximately $1.5 \times 10^5$ spores/ml) of the fungus and incubated for 36 hours at a high atmospheric humidity and at a temperature of 23°C. The incubation is then continued at normal atmospheric humidity and at from 22° to 23°C. At 7-8 days after

the infection, the protective effect is assessed on the basis of the fungal infestation.

Compounds from Tables 1 to 6 exhibited a good effect against Colletotrichum. Thus, the compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46, for example, reduced fungal infestation down to 0 to 20 %. By contrast, infected control plants, whose seeds have not been treated, exhibited a 100 % infestation with fungus.

Example 3.14: Residual protective effect against Venturia inaequalis on apple shoots
Apple cuttings having fresh shoots of 10-20 cm in length are sprayed with a spray liquor (0.02 % active substance) which has been prepared from a wettable powder of the active compound. After 24 hours, the treated plants are infected with a conidial suspension of the fungus. The plants are then incubated for 5 days at 90-100 % relative atmospheric humidity and placed in a greenhouse at 20-24°C for a further 10 days. Scab infestation is assessed 15 days after the infection.

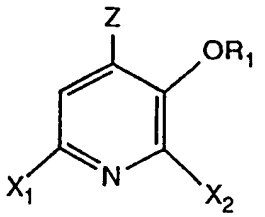
Compounds from Tables 1 to 6 exhibited a protective effect against infestation with Venturia. By contrast, untreated but infected shoots exhibited a 100 % infestation with Venturia.

Example 3.15: Effect against Cercospora nicotianae on tobacco
8 week-old tobacco plants are treated with a formulated solution of the active compound (concentration: 200 ppm). 4 days after treatment, the plants are sprayed with a spore suspension of Cercospora nicotianae (approximately $10^5$ spores/ml) and incubated for 5 days at high atmospheric humidity and at a temperature of 22°-25°C. The incubation is then continued at normal atmospheric humidity and at 20°-22°C. 12-14 days after the infection, the symptoms are then assessed on the basis of the fungal infestation.

Compounds from Tables 1 to 6 exhibited a good effect against Cercospora. Thus, compounds 1.1, 1.2, 1.12, 1.13, 1.29, 1.30, 1.31, 1.623, 1.624, 1.625, 2.1, 2.2, 3.109, 3.145, 3.181, 3.190, 5.1, 5.10, 5.19, 6.1, 6.10, 6.19 and 6.46, for example, reduced the fungal infestation down to 0 to 20 %. Infected control plants exhibited a 100 % infestation with the fungus.

WHAT IS CLAIMED IS:

1. A compound of the formula I



(I)

in which:

$X_1$ is halogen or hydrogen,

$X_2$ is halogen;

Z is -C(=O)A, -C(=S)A or $-CH(OR_2)_2$, and in which

A is hydrogen, $OR_3$, $SR_3$, $NR_4R_5$, $NHOR_6$, $-ON=CR_7R_8$ or $NH-N(=C)_n(R_9)R_{10}$;

$R_1$ is hydrogen; $C_1$-$C_4$alkyl which can be unsubstituted or substituted by phenyl, -C(=O)O$C_1$-$C_2$alkyl, -C(=O)Obenzyl, $C_1$-$C_3$alkoxy, phenoxy, -C(=O)-$C_1$-$C_3$alkyl or -C(=O)phenyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once or twice by halogen and/or methoxy; -C(=O)-$C_1$-$C_8$alkyl which can be unsubstituted or substituted by phenyl, -C(=O)O$C_1$-$C_2$alkyl, $C_1$-$C_3$alkoxy, phenyloxy, benzyloxy or -OC(=O)-$C_1$-$C_3$alkyl; -C(=O)phenyl, where the phenyl radical can be unsubstituted or substituted once or twice by halogen, hydroxyl, methoxy, trifluoromethyl or trifluoromethoxy; -C(=O)N($C_1$-$C_2$alkyl)$_2$; -C(=S)N($C_1$-$C_2$alkyl)$_2$; -$SO_2$-$C_1$-$C_2$alkyl; -$SO_2$-benzyl or -$SO_2$-phenyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once or twice by halogen, hydroxyl, methoxy, trifluoromethyl or trifluoromethoxy; or -$SO_2$-$NR_{15}R_{16}$;

$R_2$ is $C_1$-$C_4$alkyl which can be unsubstituted or substituted by phenyl, $C_1$-$C_2$alkoxy, phenoxy or benzyloxy; $C_1$-$C_4$acyl; or a cyclic 5 to 6-membered acetal which can be unsubstituted or substituted by $C_1$-$C_3$alkyl, hydroxyl or benzyl;

$R_3$ is hydrogen; a singly to triply charged metallic cation, or $NH_4^+$; $C_1$-$C_8$alkyl which can be unsubstituted or substituted once to three times by halogen, $C_3$-$C_6$cycloalkyl, $C_1$-$C_4$alkoxy, phenoxy, benzyloxy, hydroxyl, carboxyl, C(=O)O$C_1$-$C_4$alkyl or C(=O)Obenzyl; $C_3$-$C_6$alkenyl; $C_3$-$C_6$alkynyl; $C_3$-$C_6$cycloalkyl; phenyl, benzyl or phenethyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once to three times by halogen, $C_1$-$C_4$alkyl, hydroxyl, $C_1$-$C_2$alkoxy,

trifluoromethyl or trifluoromethoxy; -C(=O)-$C_1$-$C_4$alkyl; -C(=O)phenyl; or a 5- or 6-membered heterocycle having one to three heteroatoms selected from N, O and S;
$R_4$ is hydrogen; $C_1$-$C_8$alkyl which can be unsubstituted or substituted once to three times by halogen, $C_3$-$C_6$cycloalkyl, $C_1$-$C_4$alkoxy, phenoxy, benzyloxy, hydroxyl, carboxyl, C(=O)O$C_1$-$C_4$alkyl or C(=O)Obenzyl; $C_3$-$C_6$alkenyl; $C_3$-$C_6$alkynyl; $C_3$-$C_6$cycloalkyl; phenyl, benzyl or phenethyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once to three times by halogen, $C_1$-$C_4$alkyl, hydroxyl, $C_1$-$C_2$alkoxy, trifluoromethyl or trifluoromethoxy; -C(=O)-$C_1$-$C_4$alkyl; -C(=O)phenyl; or a 5- or 6-membered heterocycle having one to three heteroatoms selected from N, O and S;
$R_5$ is hydrogen, $C_1$-$C_6$alkyl or benzyl; or
$R_4$ and $R_5$ form, together with the nitrogen atom, a cyclopentylamine, cyclohexylamine, morpholine or dimethylmorpholine ring;
$R_6$, $R_7$, $R_8$, $R_9$ and $R_{10}$ are hydrogen, $C_1$-$C_6$alkyl, phenyl or pyridyl, where the phenyl radical or pyridyl radical can be unsubstituted or substituted once to three times by halogen, $C_1$-$C_4$alkyl, hydroxyl, $C_1$-$C_2$alkoxy, trifluoromethyl or trifluoromethoxy;
n is 0 or 1; and
$R_{15}$ and $R_{16}$ are hydrogen, $C_1$-$C_4$alkyl, phenyl or benzyl.

2. A compound of the formula I according to claim 1, wherein $X_1$ and $X_2$ are halogen.

3. A compound of the formula I according to claim 2, wherein Z is -C(=O)A or -C(=S)A.

4. A compound of the formula I according to claim 3, wherein A is hydrogen, $OR_3$, $SR_3$ or $NR_4R_5$.

5. A compound of the formula I according to claim 4, wherein both $X_1$ and $X_2$ are either chlorine or bromine,
Z is -C(=O)A;
A is hydrogen, $OR_3$, $SR_3$ or -$NHR_4$;
$R_1$ is hydrogen, $COCH_3$ or benzoyl; and
$R_3$ and $R_4$ are hydrogen, $C_1$-$C_8$alkyl which can be unsubstituted or substituted once to three times by halogen, $C_3$-$C_6$cycloalkyl, $C_1$-$C_4$alkoxy, phenoxy, benzyloxy, hydroxyl, carboxyl, C(=O)O$C_1$-$C_4$alkyl or C(=O)Obenzyl, $C_3$-$C_6$alkenyl, phenyl or benzyl, where the respective phenyl radicals of these substituents can be unsubstituted or substituted once to three times by halogen, hydroxyl, methoxy, trifluoromethyl and/or trifluoromethoxy; and

$R_5$ is hydrogen.

6. A compound of the formula I according to claim 2, wherein $X_1$ and $X_2$ are chlorine, Z is COOH, $COOCH_3$ or COObenzyl; and
$R_1$ is hydrogen or $COCH_3$.

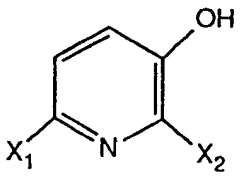
7. A compound of the formula I according to claim 3, wherein A is $NHOR_6$, $ON=CR_7R_8$ or $NH\text{-}N(=C)_n(R_9)R_{10}$.

8. A compound of the formula I according to claim 1, wherein Z is $-CH(OR_2)_2$.

9. A process for preparing a compound of the formula III, in which $X_2$ is Cl, which comprises reacting a 3-hydroxy-2-oxo-1(2H)-pyridinesulfonic acid alkali metal salt with thionyl chloride or phosgene in an inert solvent or solvent mixture at from room temperature to 150°C.

10. A process for preparing a compound of the formula III, in which $X_2$ is F, which comprises reacting a mixture of pyridine, hydrogen fluoride and sodium nitrite with 2-amino-3-pyridinol at a temperature of from -78°C to 25°C.

11. A compound of the formula III




(III)

in which $X_1$ is hydrogen and $X_2$ is fluorine.

12. A composition for protecting plants against infestation with microorganisms, which comprises, in addition to the customary excipients and adjuvants, at least one compound of the formula I according to claim 1 as the active component.

13. A composition according to claim 12, which comprises at least one compound of the formula I according to claims 2-8 as the active component.

14. A process for preparing an agrochemical composition as claimed in claim 12, which comprises intimately mixing at least one compound of the formula I as defined according to claim 1 with suitable solid or liquid excipients and adjuvants.

15. The use of compounds of the formula I according to claim 1 for protecting plants against infestation with phytopathogenic microorganisms.

16. The use of compounds of the formula I according to any one of claims 2 to 8 for protecting plants against infestation with phytopathogenic microorganisms.

17. A process for protecting plants against infestation with phytopathogenic microorganisms, which comprises applying a compound of the formula I according to claim 1, as the active compound, to the plant or its habitat.

18. A process for protecting plants against infestation with phytopathogenic microorganisms, which comprises applying a compound of the formula I according to any one of claims 2 to 8, as the active compound, to the plant or its habitat.

19. A process for immunizing plants against infestation with phytopathogenic microroganisms, which comprises applying a compound of the formula I according to claim 1, as the active compound, to the plant or its habitat.

20. A process for immunizing plants against infestation with phytopathogenic microorganisms, which comprises applying a compound of the formula I according to any one of claims 2 to 8, as the active compound, to the plant or its habitat.

21. A process according to claim 17, wherein the phytopathogenic microorganisms are fungal organisms.

22. A process according to claim 21, wherein the fungal organisms are from the Ascomycetes, Basidiomycetes or Fungi imperfecti classes.

23. A process according to claim 17, wherein the phytopathogenic microorganisms are bacteria.

24. A process according to claim 17, wherein the phytopathogenic microorganisms are viruses.

25. The compound of the formula I, in which $X_1 = X_2$ = chlorine, $R_1$ is hydrogen and Z is COCl.

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